VEGETABLE TANNINS

E. H. W. ROTTSIEPER

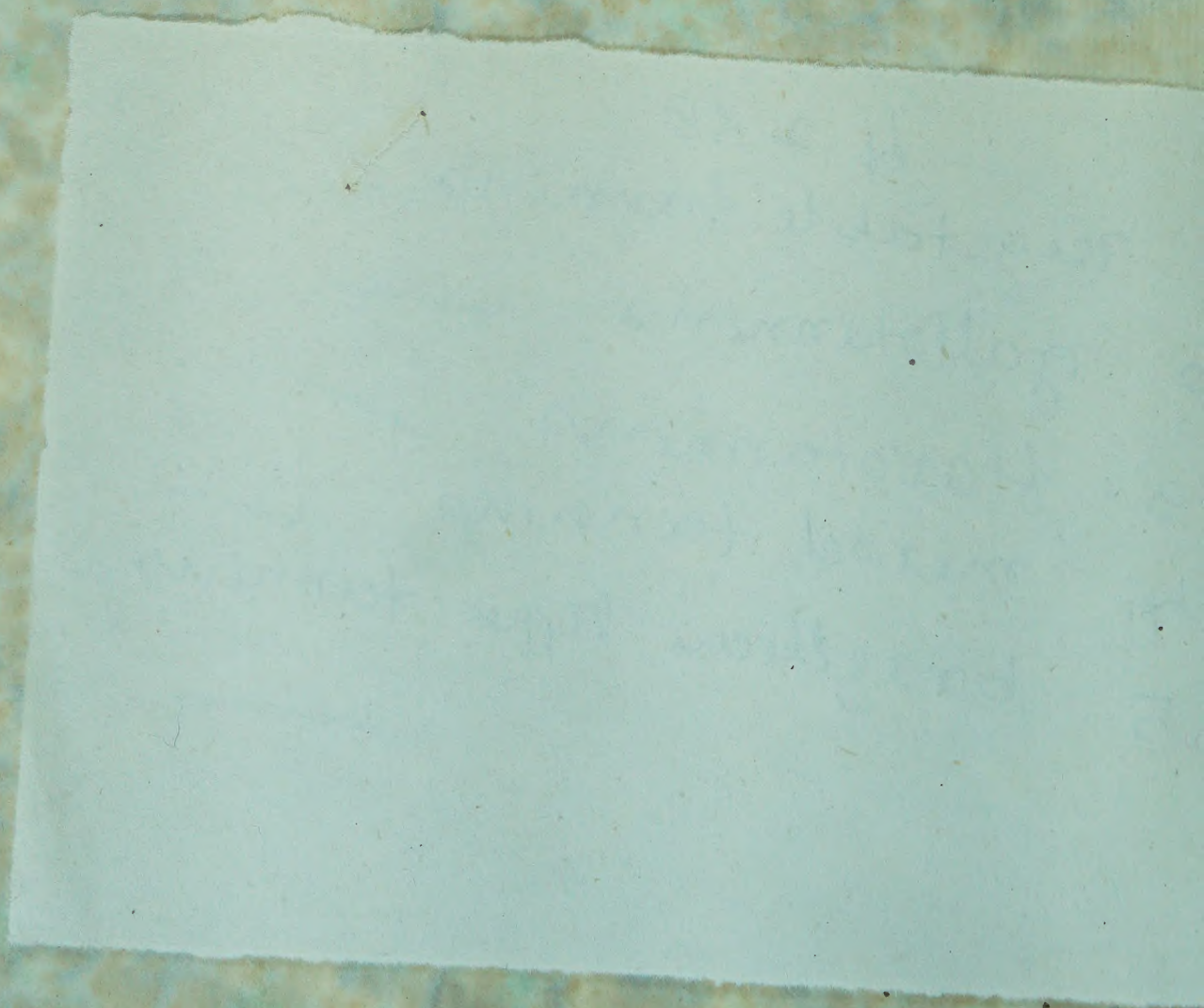To Dr. Howes
of Kew Gardens,

with the author's compliments.
19/8/49.

Central Food Technological Research Institute
Mahalla.
with the compliments of
F. N. Howes,
Royal Botanic Gardens,
Kew.
Dec. 1959.

VEGETABLE TANNINS

An Abridged Survey on the Chemical Nature of Vegetable Tannins

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PREFACE

This essay on the nature of vegetable tannins was made at the request of the Management of The Forestal Land, Timber and Railways Company, Ltd., with a view to compiling in as concise a form as compatible with the complexity of the subject, the essential facts known about the structural nature of the tannins.

An attempt was made at abstracting all the available literature. Due to war conditions and other reasons, a great many sources were not accessible and therefore many gaps will be found in the context.

The number of tanning materials included in this essay has been limited to those which have a definite commercial importance and those that are apparently capable of claiming a special scientific interest.

Another reason for writing this monograph was the desire of placing on record a number of gaps both in framework and in details, of the picture we can so far draw of some of the multitude of tannins.

The reader will no doubt notice the greater volume devoted to the flavotannins than to their opposite, viz. the gallotannins. This is certainly due mainly to the overwhelming interest our Company must have in the nature of flavotannins to which our chief products, Quebracho and Wattle belong, and to the greater experience the writer has been fortunate to gain in the realms of flavotannins. On the other hand, the latter is inclined to take the view that flavotannins offer to research a somewhat less complex picture than gallotannins and that therefore the inroads into the knowledge of their nature, are in general, deeper and wider, although the first principal efforts in tannin research seem to have been made with gallotannins.

No attempt was made at giving explanations for the tanning process and theories about the genesis of tannins in plants were only touched.

Some of the names of families, genera and species of plants have been verified by botanists to whom the writer wishes to express his very cordial thanks. A number of names, however, are still under consideration and the nomenclature employed cannot be considered final.

A short bibliography is attached at the end of the essay, together with an Appendix giving the analytical composition of specific samples of tanning materials.

Harpenden, June 1946   E.H.W.R.

CONTENTS

INTRODUCTORY

When speaking of vegetable tannins we think of organic substances which are capable of converting animal fibrous tissue into decay resisting leather. The combination of collagen and tannin is certainly at least partly, a chemical process and is as such based on the chemical nature of the tannins as well as on that of the collagen. When considering the great number of different tannins we can state a certain number of properties which are common to all of them such as :—

A high molecular weight, causing colloidal properties without, in general, producing insolubility. Tanning extracts are essentially colloidal solutions in which the tannin particles are present in all forms of dispersion, even in mechanical suspension.[1])

A great number of free phenolic hydroxyl groups, which are mainly responsible for the solubility of tannins in water. With increasing blocking of these hydroxyl groups either by esterification or etherification or by polymerisation the solubility is reduced.

With few exceptions, all tannins are amorphous and non-crystalline and form colloidal solutions in water. The crystalline tannins have a lower molecular weight, a smaller number of phenolic hydroxyl groups and possess therefore a strongly reduced tanning capacity.

A distinct degree of acidity resultant from the polarity of the phenolic hydroxyl groups, which in some cases is enhanced by free carboxyl groups ;[2]) this acidity, i.e. the movability of the hydrogen ions is at least partially caused by the internal stress in the phenolic body and is enhanced by the accumulation of hydroxyl groups in one molecular complex. Tannins are often accompanied by free true carboxylic acids but they possess a distinct acidity of their own.

Fractionation of flavotannin extracts yields sediments with a lower pH or higher acidity than that of the supernatant liquors although the majority of any admixed soluble free true acids must have been separated.

On the other hand, polymerisation, e.g. of Quebracho tannin, which must be thought to be accompanied by blocking and inactivation of phenolic hydroxyl groups, yields products with lower acidity than that of the original tannin.

Tannins formed by esterification of carboxyl groups usually exhibit a higher acidity than those formed by condensation or polymerisation of components free from carboxyl groups. This increased acidity is perhaps caused by secondary valencies and/or a greater number of hydroxyl groups of which such tannins are possessed.

A certain degree of astringency.

Intense colouration in the presence of iron salts.

The capacity of firm and often irreversible combination with protein.

Precipitation from aqueous solution by alkaloids.

The faculty of producing an improved hydrothermostability and an increase in the tryptic resistance of the treated hide substance.

The phenolic polarity seems to be the original cause for the reactivity towards proteinic matter. The combination of the properties enumerated above produces the tanning capacity.

For the better understanding of the chemistry of vegetable tannins it seems to be appropriate to set out hereunder the formulæ of the most important building elements, or decomposition products of vegetable tannins.
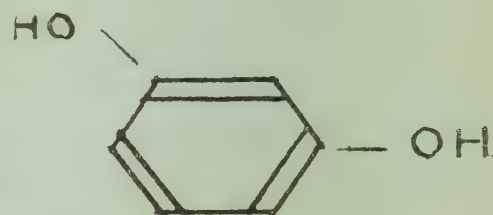
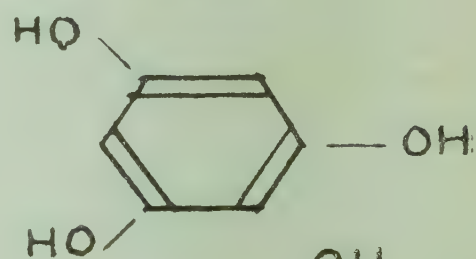Phenol = Monohydroxybenzene

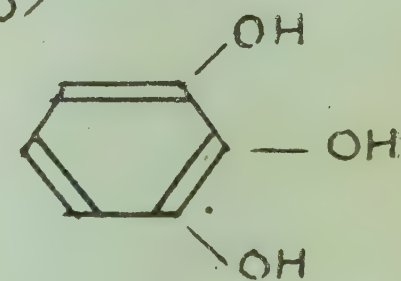Catechol = Orthodihydroxybenzene
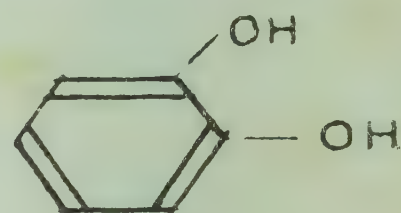
Resorcinol = Metadihydroxybenzene
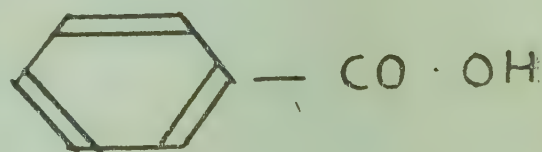
Phloroglucinol = symmetrical
    trihydroxybenzene

Pyrogallol = vicinal
        trihydroxybenzene

Acetic acid = $CH_3.CO.OH$

Benzoic acid =

Parahydroxybenzoic
        acid =

2

β-Resorcylic acid = 1,3-dihydroxybenzene-car-boxylic acid

$HO - \langle \text{benzene ring with } OH \rangle - CO \cdot OH$
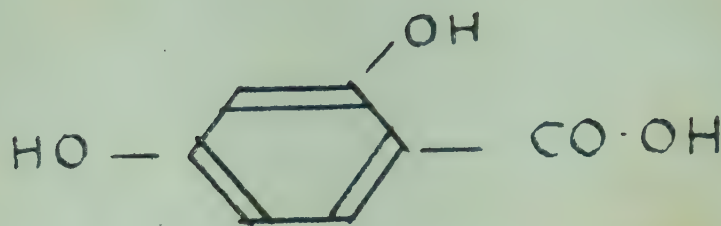
Protocatechuic acid = 1,2-di-hydroxybenzene - 4 - car-boxylic acid

$HO, HO - \langle \text{benzene ring} \rangle - CO \cdot OH$
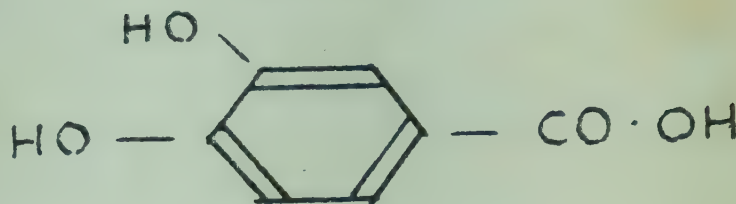
Gallic acid = 1,2,3-trihydroxy-benzene-5-carboxylic acid

$HO, HO - \langle \text{benzene ring with } HO \rangle - CO \cdot OH$

Metadigallic acid = a depside of 2 molecules of gallic acid

$HO, HO - \langle \text{benzene ring with } HO \rangle - CO \cdot O - \langle \text{benzene ring with } CO \cdot OH, HO, OH \rangle$
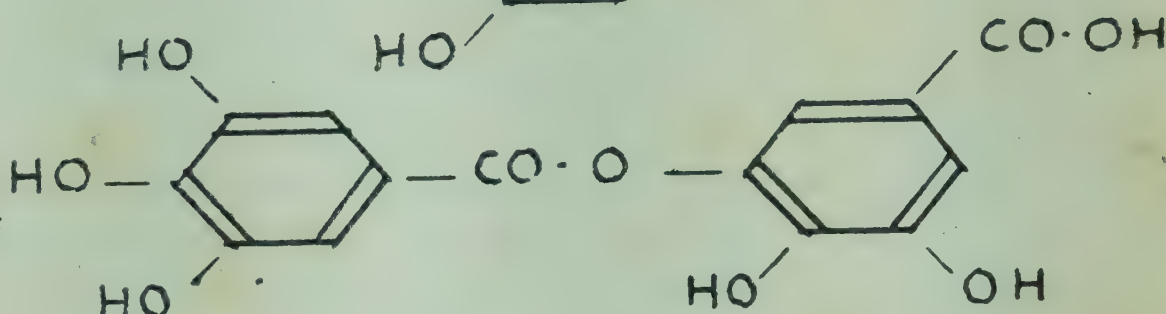
Ellagic acid = an oxidation pro-duct and inter-nal di-lactone of 2 molecules of gallic acid

$HO - \langle \text{benzene ring with } CO - O, HO, O - CO \rangle - \langle \text{benzene ring with } OH, OH \rangle - OH$
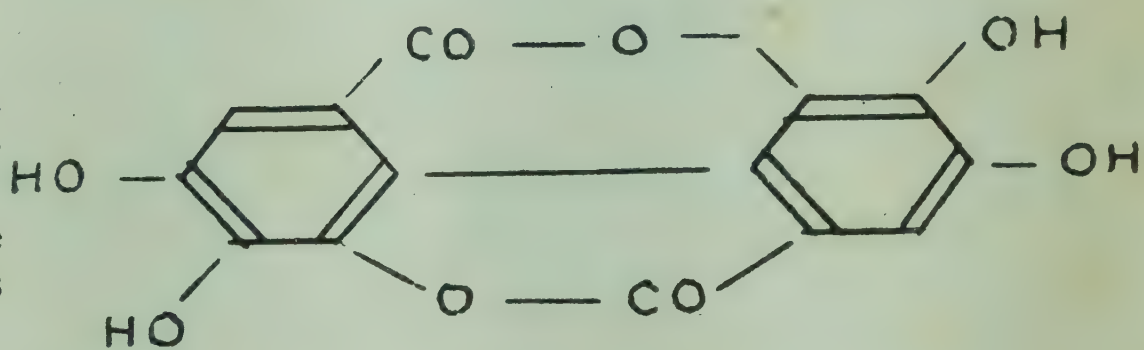
Chebulinic acid. A product of as yet unknown structure. Its molecular formula is $C_{41}H_{34}O_{27}.9H_2O$ and it consists of digalloyl-glucose, gallic acid and an unknown dibasic acid $C_{14}H_{14}O_{11}$ which may perhaps have a structure similar to the following [3]):—

```
CO·OH
 |
C = O
 |
HOC — CH(OH) — C = C — ⟨benzene ring with OH, OH, OH⟩ — OH
 |              H   H
HC·OH
 |
CO·OH
```

3
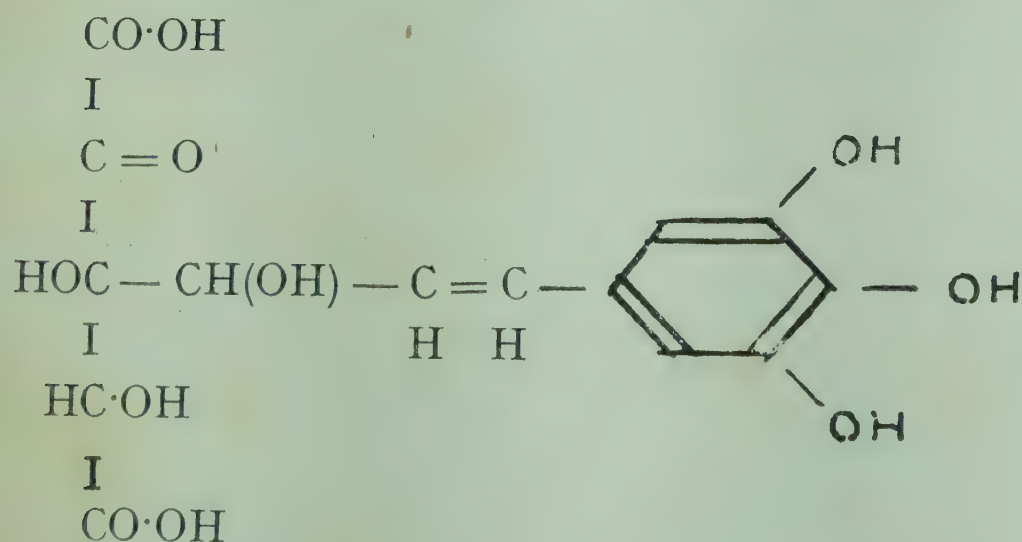
In tannery liquors, a great number of other acids may be found, which, however, do not form part of the tannin itself but may, in general, be fermentative decomposition products of tannin constituents, e.g. of sugars.

Metadigallic acid and ellagic acid may be considered to form a transition to the group of substances which are called depsides.

These are ester-like compounds in which a carboxyl group of a phenol-carboxylic acid is linked with a phenolic hydroxyl group of another molecule of phenol-carboxylic acid, either of the same or of another kind. The study and preparation of depsides has greatly helped in the investigation of the nature of the group of gallotannins, particularly of the so-called " tannic acid," i.e. the " Chinese tannin " and related substances[4]).

Digallic acid is certainly a depside. Ellagic acid could also be so called although the linking-up groups are situated in the same molecule. It is the dilactone of hexahydroxy-diphenyldicarbonic acid. In the literature it has often been referred to as a diphenyl-methylolid which name does not seem to have been very fortunately chosen.

Ellagic acid, according to Nierenstein and Perkin[5]), is accompanied by a trinuclear substance which may be considered as a depside of ellagic acid, similarly formed as ellagic acid itself. Because of its convertability by zinc dust distillation into the new hydrocarbon " Ellagene " of the constitution.
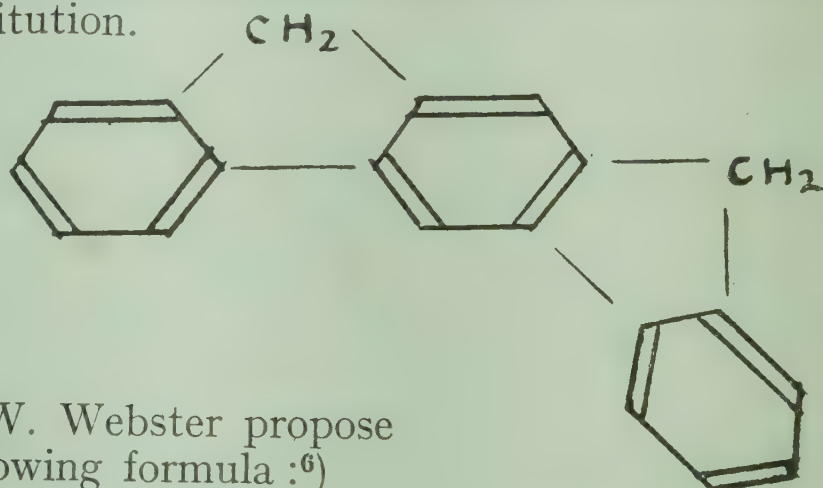
M. Nierenstein and C. W. Webster propose for the depside the following formula :[6])

4
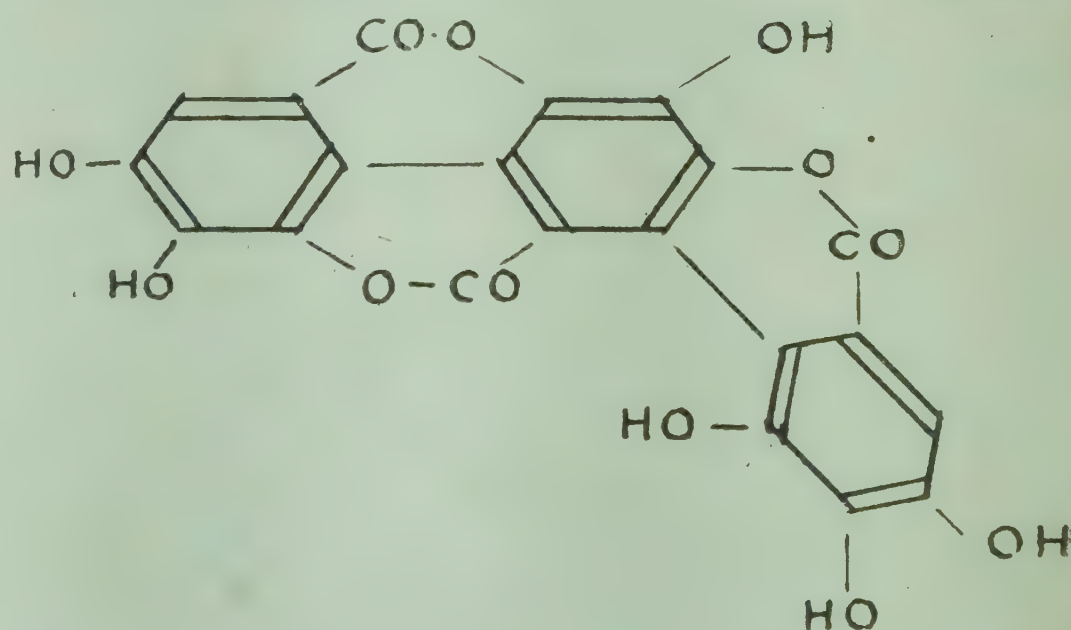
Other depsides occurring in nature are :—

Lecanoric acid =
    paradiorsellinic
    acid.
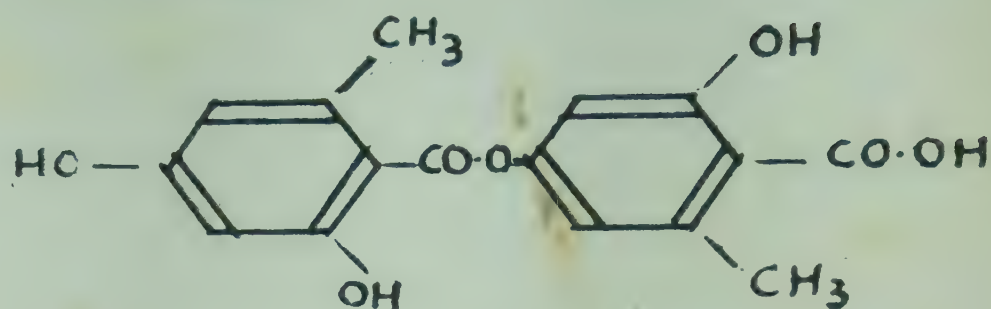
Evernic acid = mono-
    methyl ether of
    lecanoric acid.
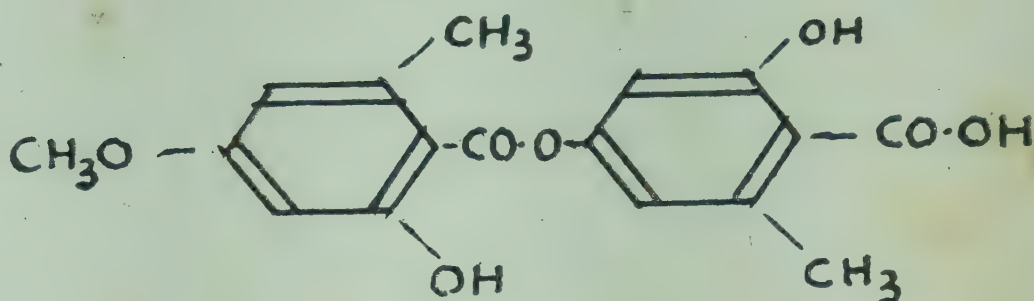
Lecanoric and evernic acids are found in lichens, the former partly free and partly as a mono-ester with the alcohol erythritol.

The lichen lecanora gangaleoides, according to T. J. Nolan, J. Keane and collaborators[7]) contains another depside, the so-called gangaleoidin which is apparently composed of two differently substituted carboxylic acids and at the same time is an internal ether thereof, in accordance with the formula :
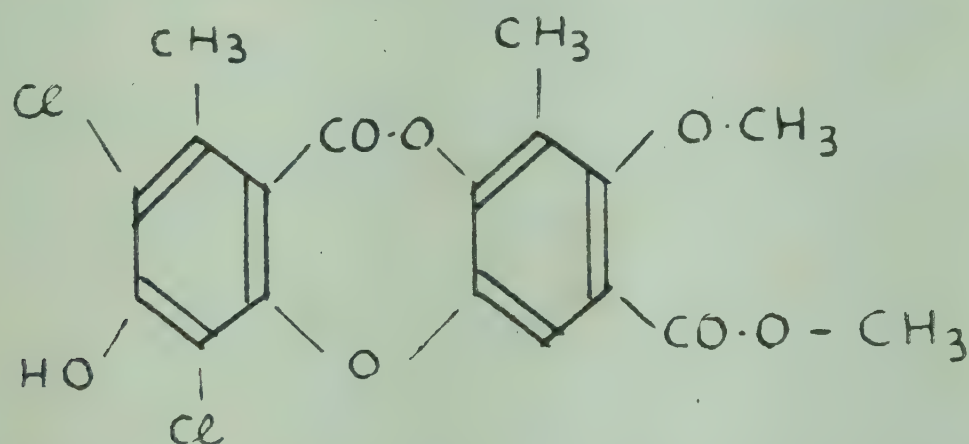
According to T. R. Seshadri, lichen depsides arise from $2:3:5:1$—CHO—$C_6H_2(OH)_2.CH_2OH$, which originates from an aldol condensation between a hexose and a biose with elimination of water.[8])

Chlorogenic acid, composed of caffeic acid and quinic acid. Caffeic acid is 3, 4-dihydroxycinnamic acid ; and quinic acid is 1,3,4,5-tetrahydroxycyclohexane-l-carboxylic acid. The structure of chlorogenic acid, according to Freudenberg, is as follows [9]) :—

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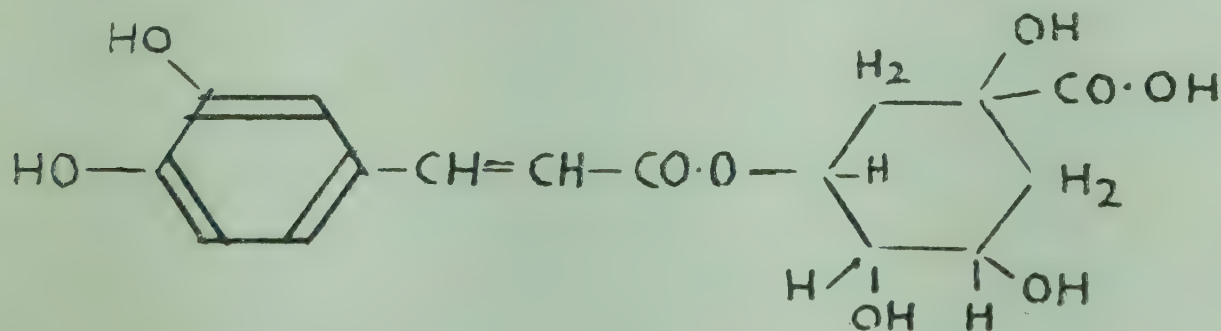
Chlorogenic and caffeic acids are widely occurring substances forming constituents of a great variety of plants. The potassium salt of chlorogenic acid is found in coffee beans and is therein combined with a molecule of caffeine.[10]) Caffeic acid occurs for instance in Yerba mate (*Ilex paraguayensis*) which contains a substance that on hydrolysis yields caffeic acid.[11])

The depsides are, in general, not tannins, they do not even precipitate gelatine from its solution, but some of them, e.g. digallic acid form actually part of some true tannins.

Furthermore, catechins and related compounds must be mentioned as building elements in the structure of the flavotannins, and forming the basis for dyestuffs very often encountered in tanning materials.

Flavane =
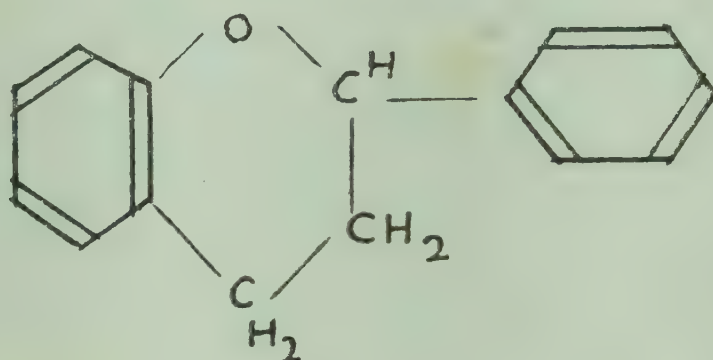
and as one example of catechins:

Gambier-
    catechin =
pentahydroxy-
    flavane
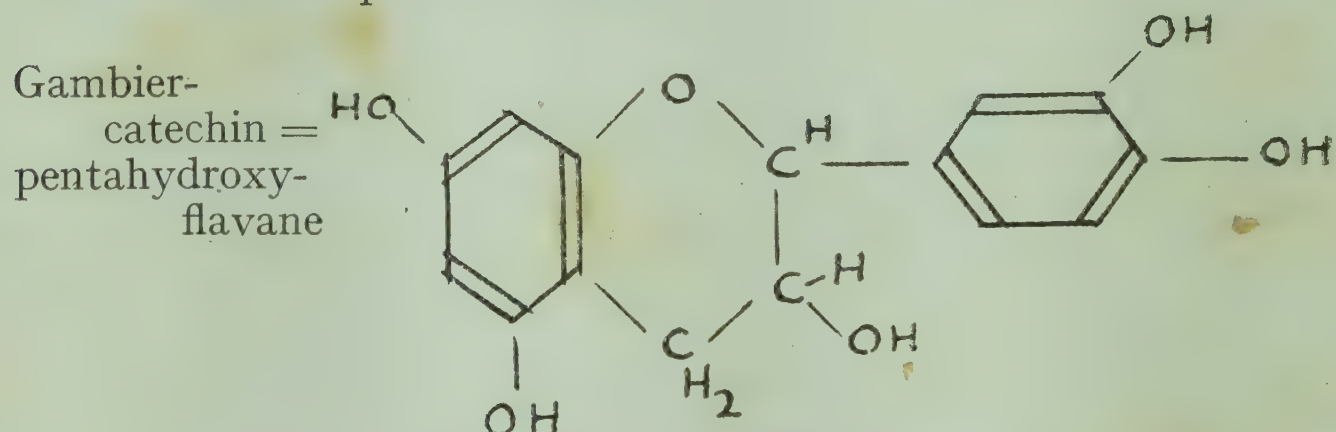
There exist several types of catechins, quite apart from the isomers caused by asymmetric carbon atoms.

There are also quite a number of dyestuffs present in tannin-containing plants, of which dyestuffs, quercetin corresponds to the abovementioned gambier catechin

Quercetin =   tetrahydroxy
                                                                    =flavonol

6
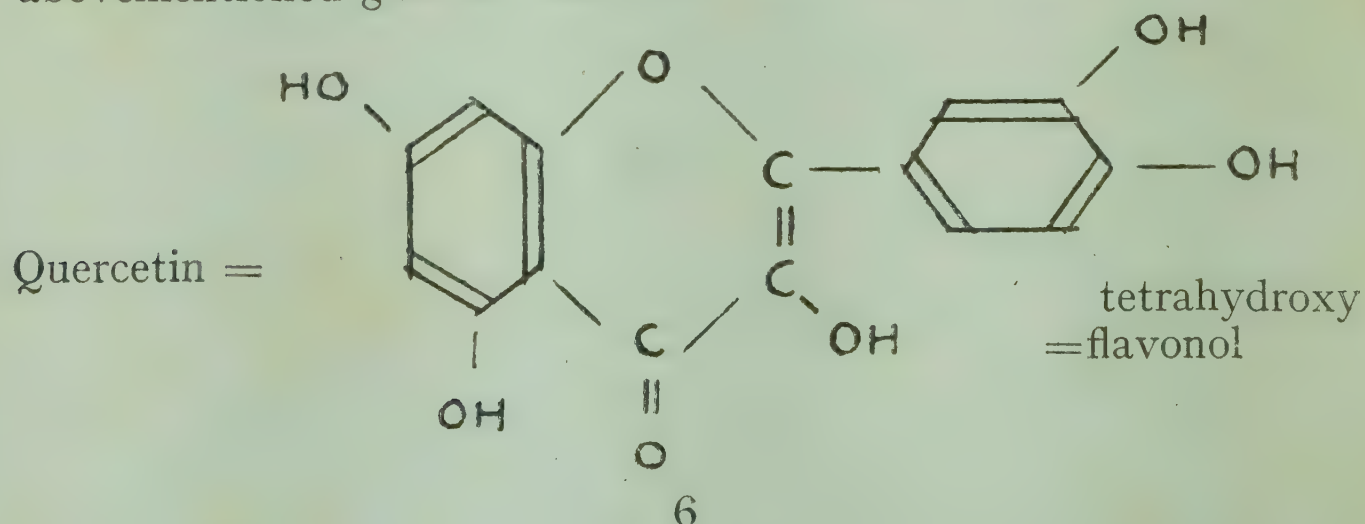
The natural vegetable tannins are usually classed either as so-called " Pyrogallol Tannins " or so-called " Catechol Tannins " in accordance with the chemical compound they generate on heating, i.e. whether pyrogallol or catechol is produced. This way of distinguishing them was good enough so long as members of the two respective classes always yielded the correct product. This latter premise is to-day not any longer true. Some tannins belonging to the catechol class, do not yield catechol but resorcinol or phenol or even pyrogallol. On the other hand, some pyrogallol tanning extracts containing dyestuffs of the anthoxanthidine group yield a slight amount of catechol in addition to a large quantity of pyrogallol.

Whilst this method is based on the products of decomposition, a more scientific method might be based either on the general chemical structure or on the behaviour towards chemicals, in particular, mineral acids.

By heating with acids, one group of tannins is hydrolysed and, in general, sugars and gallic acid are split off. This group is therefore called " hydrolysable tannins."[12] : they are more or less the same as comprised in the term " pyrogallol tannins." The other kind of tannins on heating with acids, yields insoluble products, coloured red and brown, called " Reds " or phlobaphenes. They are therefore also called " phlobatannins " which term covers more or less the meaning of the former name " catechol tannins." This second class of tannins very often contains insoluble or partly insoluble phlobaphenes when still in their natural place of origin, i.e. in the plant. The phlobaphenes are not only formed on heating with acids. They may also be formed on heating with water only, at higher temperatures or by treatment with strong acids at lower temperatures and even by direct solar irradiation only.

By reason of their easy condensability with aldehyde and acid the phlobatannins might be called " condensable tannins." Because they are not single units, but caused by " condensation " (and probably dehydration) of several units to the larger complex, K. Freudenberg calls them " condensed tannins." [12]

The usual practical method of distinguishing between the two classes of tannins is carried out by heating the analytical solution of the extract with hydrochloric acid and formaldehyde solution, by which the phlobatannin is condensed and precipitated, whilst the hydrolysable tannin is mainly kept in solution and may, if present, be recognised by the blue-black colouration of the partly neutralised filtered solution when treated with ferric salts.[13]

In this reaction all phlobatannins are thrown out of solution and also some constituents contained in the solution of the other class of tannins, e.g. dyestuffs which, without being tannins possess a chemical structure similar to that of the phlobatannins. That is partly the reason why some so-called pyrogallol tannins e.g. chestnut, when heated with acid and formaline yield a small but appreciable amount of precipitate.

7

When considering the chemical structure of the various tannins we should distinguish between "Gallotannins" on the one hand, i.e. such tannins as are derived from gallic acid or derivatives thereof and, on the other hand, "Flavotannins," i.e. tannins which are derived from Flavane.

The first class could also be called Ester-tannins, as they are mainly ester-like compounds of gallic acid, digallic acid or ellagic acid with sugars, e.g. glucose, whilst the second class could be called "Catechin-tannins" [14]) because they are polymerisation and dehydration products of catechin or other compounds of similar structure.

In general, the knowledge of the chemical nature of tannins has not advanced very far. Some of them can definitely be classed as Gallotannins and some as Flavotannins, whilst a number, for the time being at least, must be termed "Mixed Tannins." A very few tannins cannot be brought under any of the above headings, they are built up in a way similar to the Flavotannins, but have their second benzene ring attached in a different manner. These are of the Brazilin type. In addition there are great varieties of tannins about the nature of which very little is known.

Several theories have been advanced on the formation of tannin in the plant and also on the part tannin plays in its life. The complexity of the problem is at least as great as that of the chemical nature of tannin. The following few examples may perhaps illustrate this.

According to E. Michel-Durand,[15]) tannins are produced when complex carbohydrates and proteins are breaking down. It is not possible to state definitely that tannins originate only from proteins or only from carbohydrates. It is quite clear that the tannins which form in the buds and the bark of the chestnut in autumn are of carbohydrate origin.

F. Vignolo-Lutati[16]) suggested that the formation of compounds in heart wood such as fisetin occurs during the death of cellular plasma and is analogous to the formation of lignin.

R. Wasicky[17]) carried out experiments which in his opinion indicated that catechins occur in the wood only after a certain period. The conditions existing in old heart wood were apparently similar to those in bark where catechins and amorphous tannins exist together.

A. Frey Wissling[18]) formulated a theory on the formation of tannins in plants on the basis of decarboxylation and deamination of amino acids with recombination of some of the decomposition products. Parts of the latter that do not combine again are excreted.

With regard to tannins in galls, Aziz Alpaut,[19]) in an article "On a few galls from Pamuclu-Valley near Ankara," expresses the opinion that it is not the tree itself that is mainly responsible for the formation of the tannins, but the specific stimulus exerted by the insect which causes the growth.

8

According to Macgregor Skene, tannins can in many instances be regarded as waste products of metabolism, whilst in some instances tannins have been proved to play a part in the metabolism. Tannins may also be found in photosynthetic organs, but are not direct products of photosynthesis. They can be formed quite independently of photosynthesis.[20]

In some instances, tannins seem to form complexly built compounds with resins or pectin or even with protein. R. Lemesle states that in older stems of Drimys Winteri Forst. the tannin which originally contained ellagic and gallotannic acid was found to have undergone partial oxidation and the tannin-resin complex to have fixed protein so as to give a product which was insoluble in water, alcohol and alkali.[21]

The same author found an alcohol-insoluble tannin-pectin complex in the cell vacuoles of Ephredra distachya L.[22] and some tannin-mucilage complexes in the pericycle of twigs and in the leaves of Gingko biloba L.[23] [24] Some varieties of nutmeg contained similar products.[23] A resin-tannin complex was found by R. Lemesle in cortex, cork and central cylinder of Sargentodoxa cuneata Rhed and Wils.[25]

In other plants alkaloids may be combined with Tannins. This may perhaps be the case in the bark, wood and leaves of White Quebracho = Aspidosperma Quebracho blanco Schlecht of the family Apocynaceae.

A theory suggested by K. Freudenberg on the formation of lignin is explained further below, in connection with flavotannins.[26]

The principal uses for which tannins have been employed already for ages are the manufacture of leather and ink, the mordanting and dyeing of textiles and fishing nets,[27] and the clarification of beer, wine and sugar solutions. There are, however, a number of other applications where tannins, particularly in recent years, have been used, such as the following :—

Manufacture of base-exchange materials or decolourising agents by aldehyde-condensation[28] or by carbonisation either with dehydrating agents, or by heating with dilute acids, particularly under pressure and at elevated temperatures.[29]

Manufacture of plastics by aldehyde-condensation.[30]

Drilling of oil wells.[31]

Boilerwater treatment.[32]

Purification of gasolene.[33]

Inhibition of oxidation of mineral oils.[34]

Separation of minerals by means of flotation.[35]

9

GALLOTANNINS

General.

This is the class of tannins usually called " pyrogallol tannins " or " hydrolysable tannins." In nature they are not always free from flavotannins. Sometimes both classes are found simply mixed together, sometimes probably they may be chemically interlocked and the single tannin unit may be represented as an ester of a catechin with a carboxylic acid. Frequently, they are accompanied by dyestuffs which are definitely derived from flavane and therefore react with acids or with acids and aldehyde just as a flavotannin. In some cases, condensation products are present, the nature of which is unknown.

Our understanding of this class of tannins has not yet been developed very much.

The principal work in this group has been conducted by E. Fischer who established the general constitution of Chinese Tannin. This work has been fundamental to all future research.[36]

As far as the present knowledge goes one can subdivide them into bloom-forming tannins and such as do not possess this property. The bloom found on and inside leather tanned with this first group consists in the majority of cases, of ellagic acid.

The tannins yielding bloom have therefore been called " Ellagitannins," a somewhat misleading term as some of the other gallotannins that do not form bloom, also contain ellagic acid.

M. Nierenstein[37] believes that there are at least two types, if not three types of ellagitannins, viz. the tannins of the Myrabolam type, those of the Knoppern type and possibly the galloyl derivatives of ellagic acid; he states that all of these types yield ellagic acid on hydrolysis.

GALLOTANNINS WITHOUT BLOOM-FORMING CAPACITY.

Principal Types.

The so-called Tannic acid and related tannins.
Sumac tannin.
Valonia oak gall tannin.
Tea tannin.
Tara.

Tannic acid and related tannins.

The following belong to this group:
    Tannic acid or Chinese Tannin.
    Turkish Tannin.
    Hamamelis Tannin.
    Acer-Tannin.
    Glucogallin.

Tannic acid or Chinese Tannin.

Up to 77% in Chinese Galls produced by the green fly Aphis chinensis on the leaves of Rhus chinensis Mill. (*R. semialata* (*Murr*.) var. *Osbecki*) of the family Anacardiaceae.

According to E. Fischer and collaborators, Chinese Tannin is principally penta-metadigalloyl—glucose, i.e. a sugar, five hydroxyl groups of which have been esterified each with one molecule of meta-digallic acid. Whilst the presence of sugar in the tannin molecule and the general constitution, as for the first time shown by E. Fischer, is still acknowledged, in accordance with more recent findings, Chinese Tannin seems in the main to be tetrametadigalloylmonogalloylglucose, i.e. a sugar of which four hydroxyl groups are esterified with one molecule of metadigallic acid each, and one hydroxyl group with one molecule of gallic acid.

As Chinese Tannin is not homogenous and may by various means be split up into different fractions possessing varying degrees of rotation of polarised light, it is to be considered as a mixture of glucose esters with gallic acid, where in general, nine molecules of the latter are combined with one of the former, and wherein the gallic acid is probably mainly contained as metadigallic acid.

It is, however, possible that instead of four digallic acid radicals, less digallic acid groups are present and simultaneously one or more depside-like chains consisting of more than two gallic acid molecules.

Hydrolysis tests made by Mitchell and Nierenstein gave 7-8% dextrose. Their results indicate that Chinese tannin is not a glucoside and that the constitution assigned to it by E. Fischer is correst.[38]) According to Clifton E. Miller and L. Wait Risnig, glucose is present as an impurity, besides being a component of the tannin molecule.[39])

Turkish Tannin.

This is found in the so-called Turkish or Aleppo galls on branches and twigs of Quercus infectoria Olivier, of the family Fagaceae, caused by the Cynipid fly Cynips tinctoria. The tannin content is stated to vary between 36% and 58%. The aqueous extract contains, in addition to the tannin itself, free gallic acid and an easily soluble form, probably sugar derivative, of ellagic acid.

The tannin is stated to be built up as a polygalloyl-ellagic acid.[40] Ellagic acid carries gallic acid in depside bond. It is contained as free acid, not as lactone as it is in Algarobilla tannin. The tannin is dextrorotatory.[41]

The tannin is not homogeneous. The average composition corresponds apparently to a molecule of glucose which is esterified with five molecules of gallic acid, which may partly be present as metadigallic acid and partly as ellagic acid.

Hamamelis Tannin.

This tannin occurs in the bark of Hamamelis virginiana L. of the family Hamamelidaceae, North America. It is one of the few crystallised tannins, and may therefore be considered to be a uniform homogeneous substance. The constitution[42] of this tannin is that of an ester-like compound of a new sugar related to the hexoses (e.g. glucose) which is esterified with two molecules of gallic acid. It is thus a digalloyl-hexose, and has 6 molecules of water of crystallisation. The sugar is probably an aldose with the aldehyde group (—CH.O) as side chain in β-position.[43]

$$CH_2.OH.C.OH.CHOH.CHOH.CH_2.OH$$
$$\mid$$
$$C = O$$
$$\mid$$
$$H$$
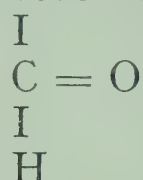
The structural picture of this tannin is likely to be as follows :[44]

13
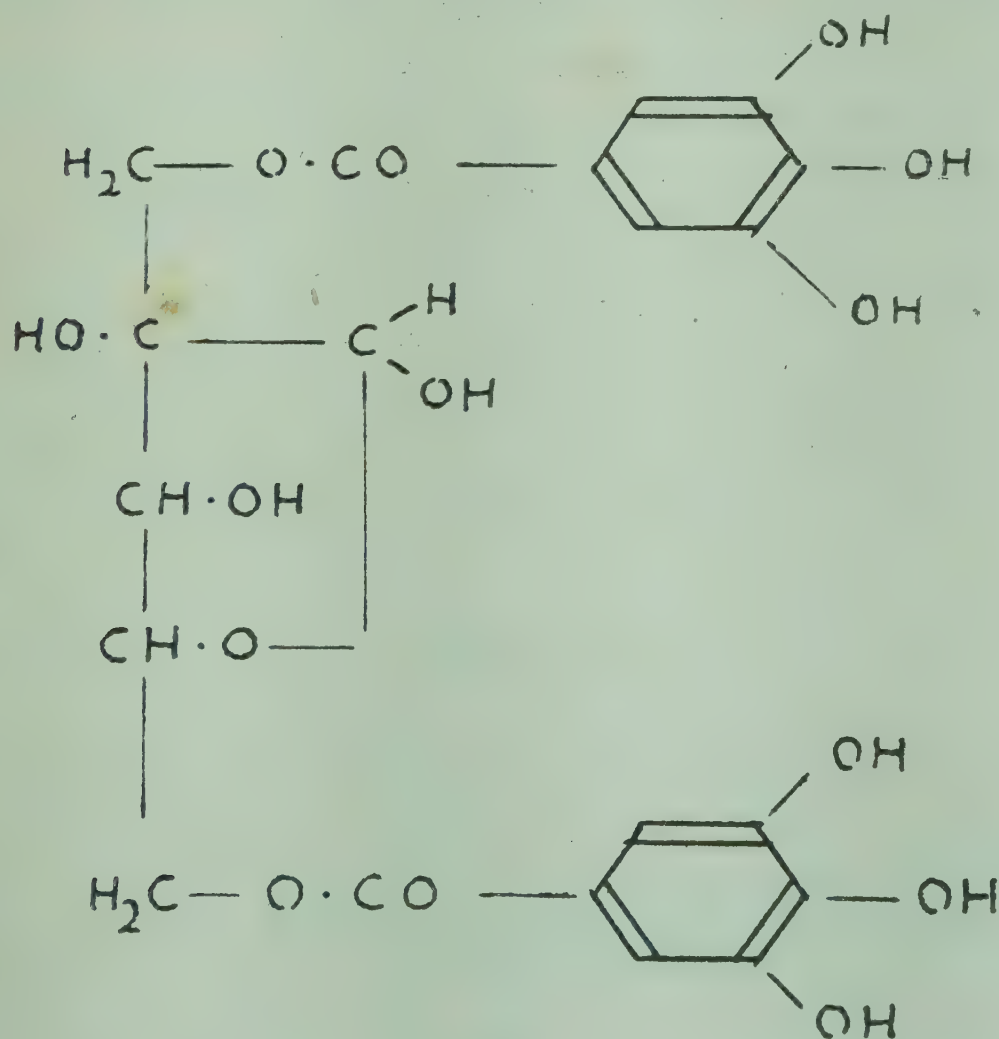
The tannin has no commercial value as a tannin particularly as its percentage in the bark is very low. The crystallised tannin constitutes approximately 1 to 2% of the bark, and there are in addition small quantities of brown non-crystalline tannins present.

According to C. P. Edwards and M. Nierenstein[45] another tannin is contained in the bark of the same plant. This tannin is called γ-Hamameli-tannin and the following formula is ascribed to it $3,4,5,1—(OH)_3C_6H_2.CO_2.(C_6H_{10}O_4.O)_2.CO.C_6H_2(OH)_2$ $—OCH_3—1,3,4,5$.

The decomposition products with hamamelase in water are stated to be gallic acid, the 3— methyl ether thereof and glucose.

The same authors found what they termed myrobalani tannin in bark of Hamamelis virginiana.[46]

Acer-Tannin.

This product[47] occurs in the leaves of a Korean maple tree, Acer Ginnala (*Maxim.*) Maxim. of the family Aceraceae. In Japan, extracts are being made containing 30% tannin which are greatly used in dyeing cotton and silk in conjunction with an iron mordant. The chemical formula of the pure tannin which is crystallised, is $= C_{20}H_{20}O_{13}$ plus water of crystallisation (2 mols).

This tannin is probably an ester of two molecules of gallic acid with one molecule of aceritol, which is an anhydrohexitol, probably derived from the hexahydric alcohol sorbitol.

The tannin is accompanied by ellagic acid, the dystuff Quercetin, and some amorphous tannin derived from aceritol. The presence of a flavonol glucoside and of a catechin is also suspected.

Another crystallised tannin was isolated from the bark of Acer spicatum Lam. Similar to Acer-tannin it contains six phenolic OH groups, which can be explained only on the assumption that the original tannin is composed of aceritol to which are attached 2 separate galloyl nuclei and not one meta- or para-digalloyl nucleus. The tannin in the bark of Acer spicatum seems therefore to be identical with the tannin in the leaves of Acer Ginnala.[48]

Glucogallin.

This substance[49] was found in Chinese Rhubarb, Rheum spec. of the family Polygonaceae, associated with catechin. It is 1-Galloyl-glucose, i.e. an ester of one molecule of gallic acid with glucose. The same plant contains another glucose ester, viz., tetrarin, in which glucose is combined with gallic acid, cinnamic acid and rheosmin, the latter compound probably being a hydroxycumin-aldehyde.

14

Glucogallin itself has the following structure :—

$$CH - O - CO - \bigodot \begin{smallmatrix} OH \\ OH \\ OH \end{smallmatrix} - OH$$
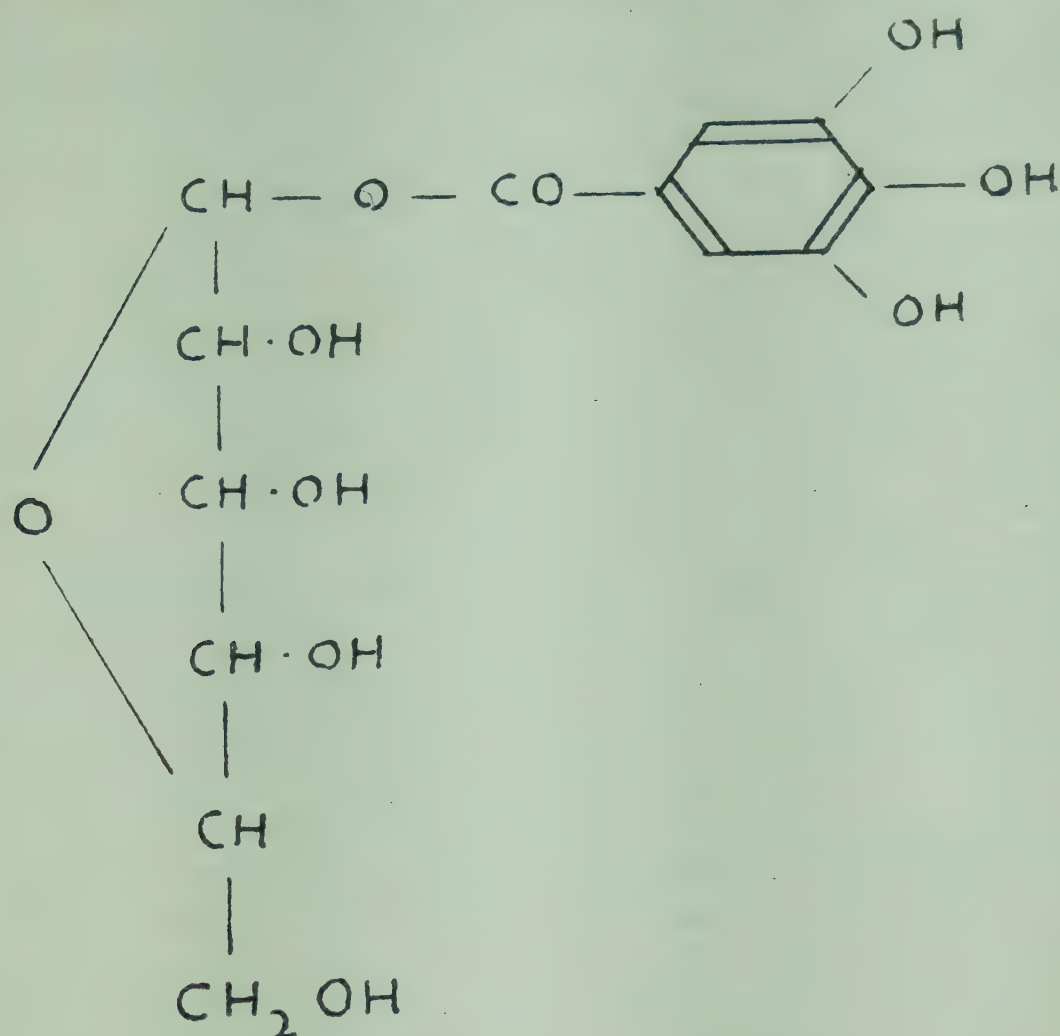
It is not a tanning material and does not precipitate gelatine. The reason is probably the comparatively low molecular weight in conjunction with the lack of phenolic polar hydroxyl groups.

A similar tannin may perhaps be present in Turkmen-Rhubarb. The roots are stated to contain 11.0 to 11.5% tannin besides 6 to 6.5% sugar, whilst the leaves are said to contain 4 to 5% tannin. Various tanning principles are said to be present, both " hydrolysing and condensed." The tanning matter, however, does not contain a phloroglucinol nucleus or ellagic acid[50] These data do not seem to give a clear picture of the class of tannin present.

Some other esters of sugar that belong into this same group have been found in plants : e.g.

Vacciniin = 6-monobenzoylglucose in Red Whortleberries[51] = Vaccinium Vitis-Idaea L. of the family Ericaceae.

two isomeric dibenzoyl-glucoxyloses in a member of the[51] family Leguminosae.

Populin = a mono-benzoylated glucoside of Salicyl alcohol in various poplar species.[51]

Violanin = a para-hydroxycinnamoyl ester of a glucoside.[51]

None of these compounds has tanning properties. The reason is the same as stated above for glucogallin. The tanning property diminishes with the increasing prevalency of the aliphatic sugar or alcohol portions and the decreasing influence of polar phenolic hydroxyl groups.

15

Sumac Tannin.

Occurs in the leaves of Rhus Coriaria L. (= Leather Sumac) of the family Anacardiaceae, Mediterranean countries, with a content of 25 to 27% tannin. A small quantity (about 0.1%) of Myricetin is present. This is a dyestuff derived from flavane, actually pentahydroxy-flavonol and belongs to those compounds that can be condensed with acid and aldehyde to an insoluble precipitate.

The tannin itself is probably mainly, but not to a homogeneous extent, pentagalloyl glucose ;[52] but another component probably participates in building up the structure. This component is not yet known as it has proved very difficult to separate and identify it.

Although no free acidic carboxyl group[53] is considered to exist in it, the purified Sumac tannin has a comparatively high acidity ; 1 gm. pure tannin is stated to require 62 ccs. N/40 NaOH.

The tannin is accompanied by free gallic acid. In contra-distinction to former statements to the effect that Sumac tannin possesses methoxy groups, modern research has found this to be not true.[54] Hydrolysis with H_2SO_4 gave 82.2% gallic acid and 8-6% sugar, with tannase 88% gallic acid and 8.2% sugar : pentagalloyl glucose would give 90.4% and 19.1% respectively. Methylation indicates that the tannin is not entirely penta-galloyl glucose.[55]

A few close relatives to Rhus Coriaria are the following : Rhus typhina L. (Staghorn Sumac). Cultivation experiments have been carried out in the United States[56] and in Germany.[57] In the latter country, Rhus typhina has been used to render the planting of Oak trees a more economic proposition than it is generally in modern times. Up to 48% tannin have been reported in leaves in controlled plantation.[57] Rhus copallina L. (Dwarf Sumac) cultivated in the United States with up to 35.8% tannin.[56] Rhus glabra L. (White Sumac) cultivated in the United States with up to 31.2%[56] Rhus cotinus L. (Venetian Sumac or Young Fustic) cultivated in Chekoslovakia.[58]

Sumac proper (Rhus Coriaria) has been cultivated in South Africa and has yielded up to 25% of tannin.[59]

Valonia Oak Gall Tannin.

It is found in gall-like excretions on Quercus Aegilops L. and other species of the family Fagaceae, Asia Minor, Greece. These growths are caused by the insect Cynips calicis. They contain on the average 30% tannin the constitution of which is probably very similar to that of the " Turkish Tannin." On hydrolysis, gallic acid is produced. The chemical structure does not seem to have been completely cleared up as yet. The tannin is dextrorotatory. Probably, ellagic acid is present in depside bond with gallic acid.[60]

16

Tea Tannin.

Leaves of Camellia sinensis (L.) O. Kuntze (Thea sinensis L.) of the family Theaceae, contain 13-18% Tannin, (Oshima found 14.1% [61]), that, on the one hand, may be interpreted as an ester of gallic acid and has therefore to be mentioned in this section, whilst, on the other hand, it appears to be closely related to the flavane tannins, in so far as the galloyl radical is connected with a catechin, and particularly probably with l-epicatechin. Furthermore, it is stated to contain free l-epicatechin and quercitrin, a dyestuff which in its turn is a rhamnoside of quercetin, i.e. an ether-like compound of the sugar rhamnose and tetrahydroxyflavonol. L-epicatechin and quercetin, as mentioned are flavane derivatives and thus related to the tannins which hitherto were called catechol tannins. The tea tannin is therefore a connecting link between the so-called " pyrogallol " and the so-called " catechol " tannins. On decomposition by heat it yields both catechol and pyrogallol.

Superior quality green tea yielded tea-catechin,[62] = gallo-catechin $C_{15}H_{14}O_7$, melting point 218°C, with astringent taste; it gave a violet colour with ferric chloride and had the characteristic phloroglucinol reaction, but gave no precipitate with gelatine. Decomposition with 50% caustic potash at 180°C for 30 minutes, of the hexa-acetyl derivative gave phloroglucinol. The methyl derivative on cautious oxidation with $KMnO_4$ in methyl alcohol formed trimethyl gallic acid.

A catechin existing in Eucalyptus occidentalis and Pistacia Lentiscus is by Freudenberg presumed to have the same formula.

A new tannin-catechin $C_{15}H_{14}O_7$ isolated by Oshima from fresh tea leaves of Formosa seems to be identical with the above.

According to W. S. Shaw and K. B. W. Jones,[63] the aroma of tea is probably due to the presence of caffeine theotannate, wherein one molecule of caffeine is combined with two molecules of " theotannin." Tea tannin is considered to be a variable mixture of tannins for which no standard formula can be proposed and in which the aliphatic side chain attached to the quercetin skeleton is especially subject to change during the growth of the plant. Theotannin treated with 10 or 20% H_2SO_4 yielded no gallic acid, but a red precipitate = " theophlobaphene."

L-epicatechin, catechin gallate and 5,-hydroxycatechin were isolated in crystalline state from various samples of tea leaves from Java.[64] From 2 to 2.5% amorphous tannin (on dry leaves) were also isolated. This gave with tannase 25.6% to 28.5% gallic acid. (5% H_2SO_4 split off only 15.2%—.) Sugar could not be detected. The amorphous tannin dissolved in water to a large extent and precipitated gelatine.

According to C. J. Harrison and E. A. Houghton Roberts,[65] tea tannin in green leaves appears to be a mixture of l-epicatechin, gallocatechin and their simpler condensation products. The galloyl

ester of epicatechin was present only in some types of leaves.

A. E. Bradfield and M. Penney in " The Chemical Composition of Tea,"[66]) mention the following phenolic substances isolated from green tea :—

Gallic acid[67])
quercetin[68])
kaempferol[69])
l-epicatechin[70])
gallocatechin[71])
l-epicatechin-gallate[72])

The fluorescence in screened ultra-violet light of cotton wool impregnated with aqueous infusion of tea leaves is very insignificant and non-characteristic.

Tara or Carabin.

Pods of Caesalpinia spinosa (Mol.) Kuntze (C. tinctoria (H.B.K.) Taub.) of the family Leguminosae, growing in Peru. The pod husks contain up to 45% and more[73]) of a valuable tannin which in certain conditions may be employed as a substitute for Sumac or Gambier to produce light leathers. The tannin is somewhat similar to, but more astringent than sumac tannin.

Probably only the existence of a comparatively high percentage of diffusion-inhibiting mucilaginous matter has prevented the tannin from wider application and has also discouraged investigation of its chemical nature of which very little is known.

Tannins of Minor Importance.

Cloves
Dhawa
Guarana
Mangue
Takaout

Cloves.

Flower buds of Eugenia Caryophyllus (Spreng.) Sprague of the family Myrtaceae. This tannin closely resembles gall-tannin. On hydrolysis it yields mainly gallic acid. Cloves are said to contain 10 to 13% tannin.[74])

Dhawa.

Leaves of Anogeissus latifolia Wall. of the family Combretaceae, India, Ceylon. Dry mature leaves contain about 16% tannin, young leaves 38%,[75]) the dry reddish tips of young leaves up to 55%.[76]) The tannin is stated to produce good pale-coloured leather.

Leaves and twigs are in India known as " Country Sumac."[76]) This tree is the main source for Gum Ghatti. The bark contains 10 to 15% tannin, one particular sample even showed 32.5%.[77])

18

Guarana.

Pods of Paullinia Cupana H.B.K. of the family Sapindaceae, Brazil, with up to 56% tannin. The seeds are stated to contain several different catechins.[78])

According to H. Gnamm, l.c., the tannin is a pure " Pyrogallol " tannin. M. Nierenstein found that the well-crystallised " Catechu-tannin " present in Guarana, on hydrolysis yielded glucose and two molecules of a carboxylic acid derived from catechin. He assigned to this tannin the formula of a glucose-depside of Gambier-catechin-carboxylic acid.

Nierenstein believes that during the manufacture of Guarana paste the above acid is produced and it is the source of d- and dl- Gambier-catechin and their respective " Catechu-tannins."[79])

Mangue.

Leaves of Laguncularia racemosa Gaertn. of the family Combretaceae, Brazil, West Indies, West Africa. 20% tannin were found. Extracts have been made with a high ash content (10-11%)[80])

The tannin is stated to contain ellagic acid.

The tannin in the bark is a flavane derivative.

Takaout or Tak'out.

Galls on twigs and flowers of Tamarix aphylla (L.) Lanza (T. articulata Vahl), of the family Tamaricaceae. Also called Ettel or Tlaia. Produced by the acarine Eriophyes Tlaiae Tarbut. North Africa, particularly in the South of Morocco and Algeria. The plant has been cultivated in the United States of America, e.g. in California and Southern Arizona.

The tannin is stated to produce very light coloured leathers which are almost white[81]).

Tannin content up to 55%,[82]) and is stated to be " pyro-gallique."

According to Em. Miège,[83]) galls from the South of Algeria yielded 0.07% catechin, by alcoholic extraction 49.95% tannin and 6.65% phlobaphenes and by extraction with potash, another 10.95% phlobaphenes.

N.B. The scanty information on the nature of this tannin does not indicate whether the tannin forms bloom or not ; but its similarity to other gall tannins justifies the tentative inclusion in this section.

Investigation of the exact nature of above 17.6% phlobaphenes is necessary.

GALLOTANNINS WITH BLOOM-FORMING CAPACITY.

The deposit on leather produced with these tannins consists, in the majority of cases, of ellagic acid.

Principal tannins of this class.

Valonia, mainly in the fruit cups and beard.
Myrabolam nuts.
Divi-Divi pods.
Algarobilla pods.
Oak wood, bark, leaves.
Chestnut wood, bark, leaves,
and a few other plants of minor technical importance, such as :—
Pomegranate fruit, bark of rhizome and twigs.
Many members of the family nymphaeaceae, e.g. nymphaea and nuphar, in the rhizome.
Hornbeam leaves.
Bistort roots.
Guayacan pods.
Cascalote pods.
The constitution of these tannins has not yet been fully ascertained, although some components have been identified. Among the latter, ellagic acid is always present. Almost in every case gallic acid was found, and in one case (Myrabolam) chebulinic acid. The tannins of this class are supposed to be glucosides, but up to the present this has not been established with certainty.

Valonia.

These are the cupulae of the oak species : Quercus Aegilops Linn. of the family Fagaceae, Asia Minor and Greece. The tannin consists probably of a mixture of galloyl-tannin and ellagi-tannin. It contains thus obviously similar ingredients to those of the " Turkish Tannin," but so much ellagic acid that it is recommended as a source for the manufacture of this acid. The tannin in Valonia is laevorotatory[84]) and probably contains a free carboxyl group.[85])

Myrabolam.

Fruits of Terminalia Chebula Retz. of the family Combretaceae, India. The tannin is laevorotatory. Only two components of the tannin are so far known besides sugar : ellagic acid and chebulinic acid. The latter is of a crystalline nature which causes the bloom on myrabolam-tanned leather to assume a crystalline structure, in contradistinction from Valonia, Divi-Divi, Chestnut and Oak.[86])

As was stated above, the chemical composition of chebulinic acid is only partly known. It seems to produce on hydrolysis, three molecules of gallic acid, one molecule of glucose and one molecule of a dibasic and probably more highly oxidised acid (containing

perhaps a trihydroxycinnamic radical) with the composition $C_{14}H_{14}O_{11}$ the structure of which is not yet known. Two molecules of gallic acid are contained as digalloyl glucose : but there exists some doubt as to whether the third gallic acid molecule is esterified with a sugar hydroxyl or whether it clings to the remaining residual acid.[86])

Chebulinic acid itself may be present in the form of a glucoside. That portion of myrabolam tannin which contains ellagic acid, possibly also forms a glucoside. The tannin itself may therefore constitute a mixture of at least two different compounds. On hydrolysis of Myrabolam tannin, gallic acid is produced which may be accounted for by the presence of chebulinic acid. Whether part of this gallic acid is present in other combination than the chebulinic acid complex is not known.

L. Reichel and E. Ulsperger ascribe to Myrabolam tannin the structure of tetragalloyl-ellagic acid.[87])

Treatment of Myrabolam extract with H_2O_2 produced a white precipitate believed to be a precursor to lignin and to be identical with Freudenberg's chebulinic acid. The equivalent was found to be 835. Half the tannin is said to be present as potassium and calcium salts. The dark substance produced on heating myrabolam extract in the presence of acid had the solubility relationships of lignin. Total lignin obtainable from myrabolam extract was determined by dissolving the dried extract in 72% H_2SO_4, yielding a yellow solution which darkened on ageing and deposited 26% of a black precipitate on dilution. Removal of this lignin did not alter the galloyl radical content of the extract nor its sugar content.[88]) The tannin is stated to be laevorotatory.[89])

Nierenstein obtained an "Ellagitannin" from myrabolams in the form of a well crystallising substance which he stated to prove on hydrolysis with emulsin, to consist of luteoic acid and two molecules of glucose, the latter preventing the closing of the luteoic acid to ellagic acid in the plant.[90])

Divi-Divi.

Pods of Caesalpinia coriaria Willd. of the family Leguminosae, indigenous to Mexico, West Indies and Northern countries of South America. The tannin which is laevorotatory[89]) is probably a mixture. It contains large quantities of free and of combined ellagic acid, besides some combined gallic acid. It is questionable whether the gallic acid produced on hydrolysis is part of the tannin containing ellagic acid or not. The presence of sugar in the tannin complex has been rendered probable. The tannin seems to contain a free carboxyl group. L. Reichel and E. Ulsperger believe it to be a tetragalloyl-ellagic acid.[87])

Very closely related to Divi-Divi are the Tari Pods or Teri Pods, the fruits of another Leguminosa, viz. of Caesalpinia digyna

21

Rottl.[91]) a native of the East Indies and not to be confused with Tara Pods (Caesalpinia tinctoria), a native of Peru. Very little seems to be known about the chemical structure of this tannin.

H. G. Biswas[92]) obtained from the ripe pods of Caesalpinia digyna a tannin with a melting point 205-212°C. (decomp.) which on hydrolysis yielded gallic acid in the proportion corresponding to the constitution of pentadigalloylglucose.

During more recent work,[93]) extraction with alcohol yielded a tannin with the same melting point which on acetylation gave a nona-acetate (melt. p. 206-208°C. under decomposition) and on hydrolysis yielded gallic acid and glucose in fair agreement with a monodigalloylglucose.

Algarobilla.

Pods of Caesalpinia brevifolia Baill. of the family Legumin-osae, Chile. The pods are said to consist of hull (21% of the pod) with 31% tannin, powder (37% of the pod) with 57% tannin and of seeds (42% of the pod) with no tannin.[94])

The tannin seems to have great similarity to that in Divi-Divi. It contains free and combined ellagic acid, both in large quantities, as well as combined gallic acid. Also here it is not yet known whether gallic acid liberated on hydrolysis forms part of the ellagitannin or not. The tannin seems to contain a free carboxyl group.[95])

M. Nierenstein stated that the pods contained methyl gallate which easily yielded ellagic acid.[96])

A glucoside seems to have been obtained in which the presence of glucose has been assumed.[97])

The tannin is dextrorotatory.[98]) According to L. Reichel, the ellagic acid is present as mono-or-di-lactone and the tannin is built up in a manner similar to that of Divi-Divi, viz. as polygalloyl ellagic acid.[99])

European Oak, Wood, Bark, Leaves.

The species growing in the Northern latitudes of Europe are Quercus robur L. (Q. pendunculata Ehrh.) and Quercus petraea (Matt.) Lieblein (Quercus sessiliflora Salisb.) and those in Southern Europe are Quercus Frainetto Ten (Q. conferta Kit.) and Quercus Cerris L. They belong to the family Fagaceae.

In the United States of America, the bark of the Chestnut oak = Quercus montana Willd. is favoured both as a tanning material and a constituent of tanning extracts.

Another Oak species of some commercial importance is the Willow oak, Quercus Phellos L. which is fairly abundant in the Piedmont area of the South-eastern United States and contains 10% and more tannin in the bark.[100])

Usually, one distinguishes between oak wood and oak bark

,tannins and states that the wood contains a pure pyrogalloltannin, whilst oak bark tannin is a mixture of pyrogalloyl and catechol tannins. This differentiation is based on the results of the hydrochloric acid-formaldehyde reaction.

It has recently been made probable[101]) that the tannin in wood and bark and also leaves is principally the same i.e. a hydrosable one or gallotannin and that the positive result (precipitate) of the above acid-aldehyde reaction with oak bark infusions is due to substances that are only admixtures to the true tannin. Such substances which may be decomposed to phloroglucinol and protocatechuic acid (potash infusion) or to catechol (distillation) are for example the dyestuff base quercetin and higher products of condensation which latter products are formed in the bark by the action of enzymes on, and by dehydration and oxydation of, the true oak bark tannin.

The tannin is stated to be also contaminated with free gallic acid and ellagic acid and with sugar and to contain free carboxyl groups itself.[102)103]) It is laevorotatory.[103])

L. Reichel and E. Ulsperger[104]) claim to have found in leaves of Quercus pendunculata, tetragalloyl-ellagic acid in acid form in the presence of catechin and catechin-like tannins. They state that the carboxyl groups of the depside in the tannins are either free or neutralised with salt formation.

Particularly the tannin in the leaves has been thoroughly studied, without, however, completely disclosing its nature. Oak tannin is stated to be amorphous. The more easily soluble portion of the tannin is said to compare, in respect of molecular weight and composition with three times a trihydroxy cinnamic aldehyde $C_6H_2.(OH)_3.CH=CH—CH.O$. Either such a product or a catechin of the pyrogallol series in more or less condensed condition appears to build up the oak tannin in conjunction with ellagic acid and sometimes with glucose (3-7%).[105])

Some authors have assumed the existence in oak tannin of a hypothetical " Quercic acid " which was thought to be free from ellagic acid but which others proved still to contain 4% thereof.[106])

Perkin and Everest[107]) differentiate between Quercitannic acid, · which is the name they give to the tannin in oak bark and Quercinic or Quercic acid which term they apply to designate the tannin in oak wood. Whilst these terms refer to the tannin as a whole in the respective materials, the name Quercic acid as used in this present monograph is merely a translation from the German term " Quercus-säure " and refers to that portion of the tannin which appears still to be of a problematic nature.

The main part of oak tannin appears perhaps to consist of a complexly built portion (perhaps called " Quercic acid) which contains gallic acid but no sugar and is itself combined on the one side with glucose, and ellagic acid on the other side in such a manner

that glucose and ellagic acid are not linked together.[108]) Gallic acid and ellagic acid may be in depside bond.[109])

"Quercic acid" showed the same reactions as oak tannin towards ferric chloride, gelatine and solvents.[110])

As may be concluded from these observations, the real nature of oak tannin still remains very much in obscurity.

One reason for this state of affairs seems to lie in the various degrees of decomposition effected by the different methods of hydrolysis, e.g. whether carried out with strong or weak acids or with strong or mild alkaline media, combined with the varying degrees of condensation in which the tannin is present at different stages of development in the parts of the plant in accordance with age, and which are probably also caused by the chemical attack.[111])

Oak tannin seems thus to supply confirmation of the belief that the tannin in the plant is seldom in the same form as we obtain it on extraction.[112])

Chestnut.

Wood, bark, leaves of Castanea sativa Mill. (European chestnut) and of Castanea dentata (Marsh) Borkh. (American chestnut) of the family Fagaceae. About the chemical nature of Chestnut wood tannins we do not know any more than about that of oak tannin. The two tannins seem to be very similar without being identical.[113])

On hydrolysis with dilute mineral acid, ellagic acid, glucose, gallic acid and quercetin have been found. Fermentation decomposition tests with emulsin yielded neither sugar nor other ingredients, with aspergillus tannase yielded a product which with sulphuric acid gave less than 3% ellagic acid ; quercetin, gallic acid and sugar were also separated and a residual substance was obtained that could not be changed by further attack with tannase or other hydrolysing agents. It constituted more than 50% of the raw mixture.[114])

The tannin in the wood is therefore apparently a mixture the principal componenet of which (structure so far unknown) contains ellagic and gallic acids, quercetin and glucose in free and combined condition. Freudenberg and Kurmeyer[115]) prepared tannin from chestnut leaves and found that there was hardly any difference between the products of decomposition of chestnut and oak leaves tannin. Of great importance was, however, the fact that chestnut tannin from the start was accompanied by less condensation products. A great significant difference was found to exist between the tannin in young leaves = "early tannin" and in fully developed leaves = "late tannin." The latter contained condensation products which seemed to inhibit or at least to render very difficult the separation of the simpler components and thus resembled very closely the oak tannin, whilst the young leaves split off the components, particularly gallic acid, much more easily.

24

W. Münz[116]) found no ellagic acid in young chestnut leaves, but 25-30% gallic acid, whilst in older leaves, ellagic acid was present. Ellagic acid is therefore probably formed from gallic acid during growth.

M. Nierenstein makes the provisional assumption that chestnut-wood tannin may be a quercetin derivative of monogalloyl-ellagic acid.[117])

The condensation products referred to above, are probably meant when A. Ponte[118]) states that the proportions of "pyrocatechol" tannins and of colouring matter are greater in the bark than in the wood.

The tannin of Chestnut wood is stated to contain free carboxyl groups.[119])

The problem culminates in the question as to whether sugar, gallic acid and ellagic acid together belong to a gallotannin which may resemble the "Turkish Tannin" and which is admixed with tannins capable of condensation or whether all these ingredients including the condensable main body belong to one larger molecule.[120])

The prickly husk of the Chestnut fruit is said to contain 10-13% of tannin.[121])

A sample of root bark from China was found to contain as much as 19.2% tannin (15.2% water) whilst the bark from the trunk had 11.1% Tan only (12.5% water).

Tannins of Minor Technical Importance.

Pomegranate.

Fruit, bark of rhizome and twigs of Punica Granatum L. of the family Lythraceae, Morocco, Spain. The dried leathery skin of the fruits contains up to 26% tannin.

Dried blossoms contained 31.2% tannin.[122]) On hydrolysis with 1.5% sulphuric acid, 54-66% ellagic acid have been obtained and in addition fermentable sugar and 2-3% of a crystalline substance which may have been gallic acid.[123])

The tannin is perhaps a mixture of glucosides of ellagic acid (mono- and possibly di-glucosides) and a minor quantity of gallic acid.

The tannin is laevorotatory.[124])

Water Lily Tannin.

The rhizomes of the species Nymphaea alba L. and odorata Ait. and of the genus Nuphar of the family Nymphaeaceae, contain a tannin that on hydrolysis with dilute acid, yields ellagic acid and seems to be similar to that in the above-mentioned three species of Caesalpinia (Divi-Divi, tari and algarobilla.)[125])

Hornbeam.

The leaves of Carpinus betulus L. of the family Betulaceae also belong to the ellagi-tannin group. Ellagic acid is split off with comparative ease from this tannin, which also yields gallic acid, but no reducing sugar. Part of the ellagic acid present is perhaps in free state and colloidally held in solution (peptised) by the tannin.[126]

Bistort.

Up to 21%[127] of tannin have been ascertained in roots of Polygonum Bistorta L. which belongs to the family Polygonaceae. The tannin on hydrolysis with 1.5% sulphuric acid, was found to split off ellagic acid and gallic acid[128] and is[129] in the plant apparently associated with gallic acid and a " phlobaphene-red." The presence of sugar seems to be doubtful. The tannin colours iron chloride green and may perhaps not be a pure gallotannin.

Bjalobrzeski,[128] on fractionation, obtained three specific tannins, Iljin[129] only two, both of which on hydrolysis with alkali yielded phloroglucinol and gallic acid. According to Iljin these two tannins are allied to oak tannin and catechu-tannin respectively.

Tannin in another species of polygonum has been investigated, viz. in Knot-grass, Polygonum aviculare, var. buxifolium Ledeb. This plant was found to contain Quercetin, as a 3-arabinoside, called avicularin ($C_{20}H_{18}O_{11}$), melting point 216°-217°. This is stated to be the first flavone or flavonol pentoside found in nature (combined with l-arabinose).[130]

Guayacan.

Caesalpinia melanocarpa Griseb. of the family Leguminosae. Argentina. The pods are stated to contain 22.5% tannin which resembles that in Divi-Divi pods.[131]

Cascalote.

Caesalpinia Cacalaco Humb. and Bonpl. of the family Leguminosae. Pods, similar to Divi-Divi, Mexico.

From 40% to 57% tannin.[132] Seems to contain sugars, as the liqours are prone to rapid fermentation.

FLAVOTANNINS

General

These are the tannins which in ordinary usage have hitherto been called " catechol tannins " or phlobatannins " and which K. Freudenberg called " condensed tannins."[133]

In contradistinction from the ester-like gallotannins, the flavotannins are probably mixtures of products of varying degrees of polymerisation and dehydration, of several molecules of catechin or catechin-like substances.

Catechin par excellence in its various forms of stereoisomeric modification has the following structure :—

a tetrahydroxyflavanol, containing two benzene nuclei and one di-hydropyrane ring.
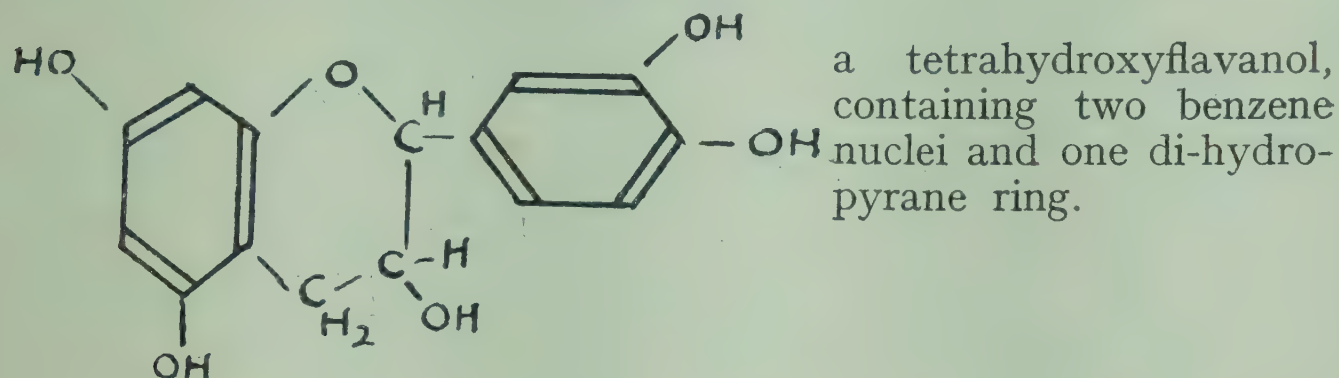
The tannins in this class are derived from simple monomolecular catechin-like basic compounds, by a kind of polymerisation in which on the one hand the oxygen bridge may be split up and one of the hydroxyl groups generated thereby reacts with an aromatic hydrogen atom of another molecule, probably that one in the 6-position, to form a carbon-to-carbon linkage between two catechin units. This method of connection may go on with a further unit and so on until various chains of different lengths have been produced.[134]

The following schedule illustrates this way of linking various units :
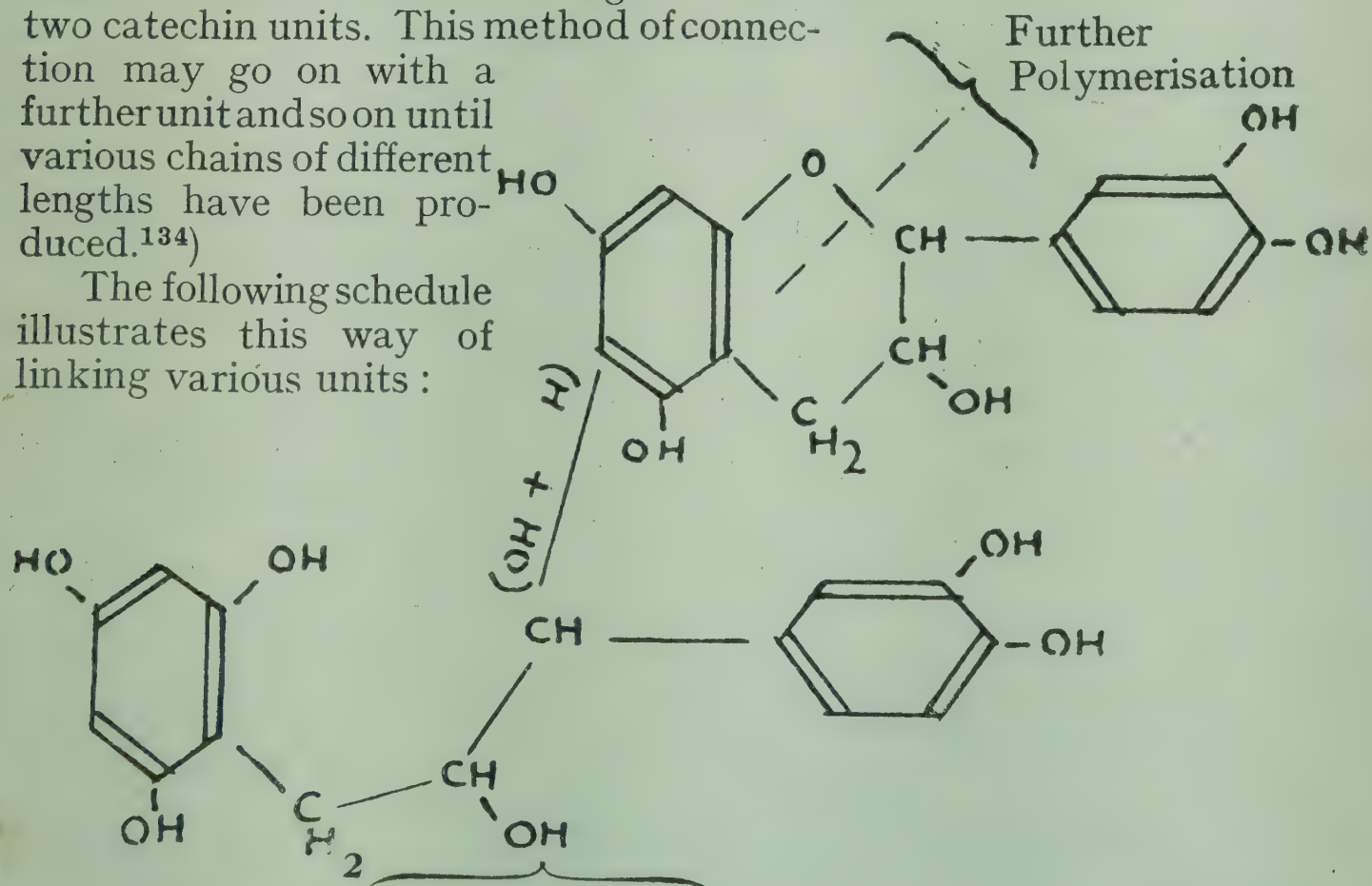
Hydroxyl group possibly partaking in secondary reaction.

27

In the same manner, further polymerisation may take place with one or more catechin units yielding products of higher molecular weight.

Secondary reactions too, by splitting off water and condensation, may play a part in the formation of the tannin.

Such secondary reactions may yield products similar to the following :—[135])
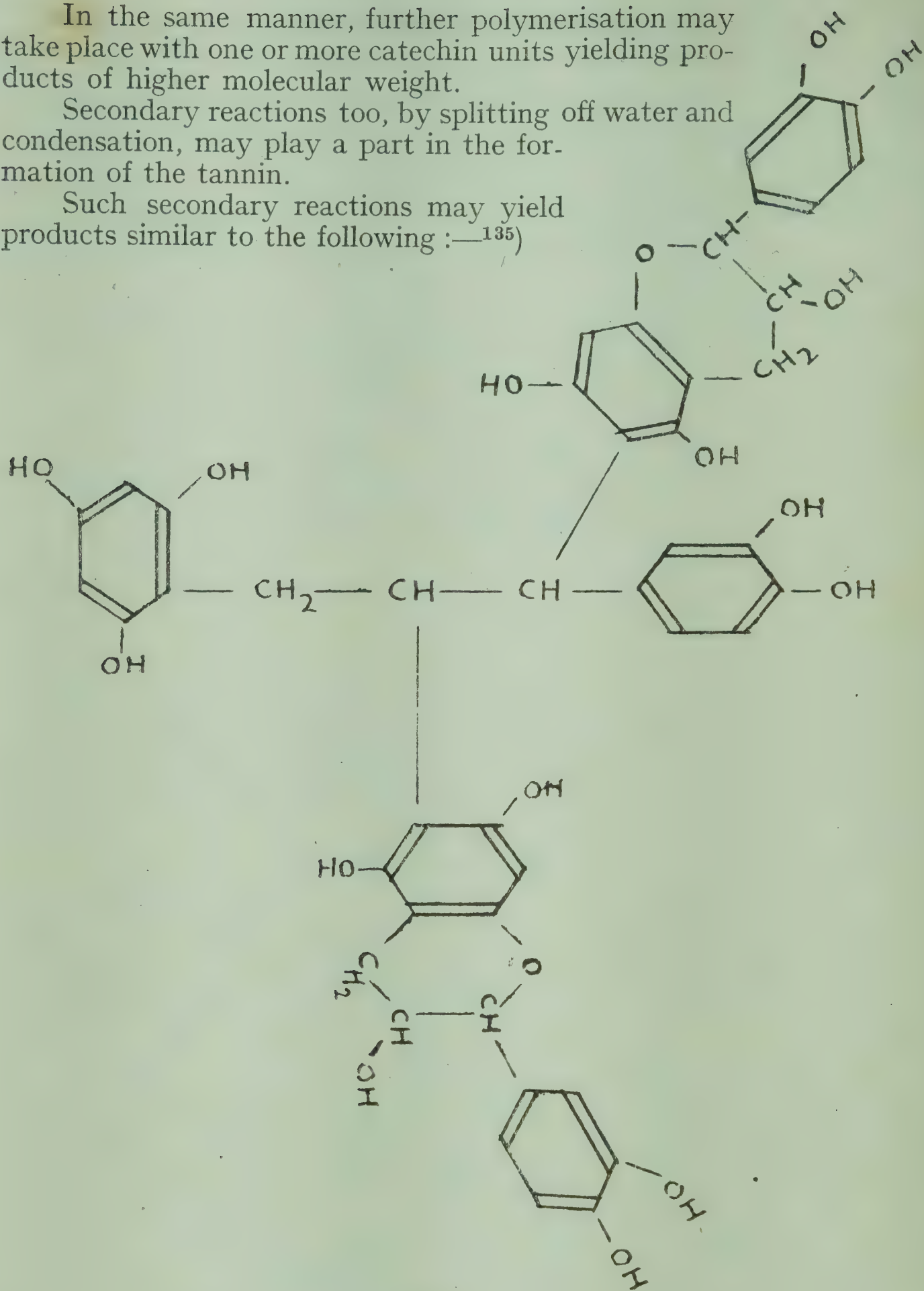
Although it has been stated[136]) that pyrane compounds with one double bond are capable of such polymerisations as demonstrated above without any alcoholic OH group being necessary, it does not seem to be proven that this alcoholic OH group may not participate in the condensation as well, or may not cause dehydration products,

28

perhaps ether-like derivatives with an aromatic hydroxyl group or producing a carbon-to-carbon condensation with a further catechin unit. The possibility of reducing viscosity and insolubility index in Quebracho extracts by prolonged heating of the liquid extracts with and without small quantities of caustic soda may point in the direction of etherification, as it is difficult to see how a C-C link could be severed by such a comparatively mild treatment after a bond had once been formed.

The continued polymerisation or condensation of a greater number of catechin units is the cause of the formation of the so-called " Reds " or " Phlobaphenes " which products with progressing increase of molecular size gradually, but completely change the character of the substance. Whilst the single catechin unit is soluble and crystalline and has no tanning property, the condensation products obtained already by heating of the aqueous solution (particularly in the presence of acids) lose the faculty of crystallising and attain the property of precipitating gelatine. The more strongly the condensation is carried out, the more intense is the tanning property which is only offset by the fact that with increasing molecular weight solubility is gradually reduced and the polar hydroxyl groups are inactivated. On heating with dilute mineral acids the formation of dark red coloured bodies proceeds rapidly which gradually lose all solubility, not only in hot water but also in aqueous alcohol and finally even in caustic alkaline solutions.[137)

This formation of " Reds " takes place in the living cell and post-mortally, when it is also accelerated by solar irradiation.

According to W. Grassmann and W. Kuntara, the biological formation of phlobaphenes is an enzymatic and oxydative process. In order to prevent undue postmortal formation of phlobaphenes, they recommend preservation of the utilisable soluble tannin by means of heating or steaming or by destroying the enzymes, as soon as possible after gathering, by enzyme poisons, e.g. hydrogen sulphide or bisulphite.[138)

There is no reason to assume that oxidation always plays a part in the formation of " Reds " particularly as the anthoxanthidine dyestuffs very often accompanying the tannins derived from the same flavane compound are more highly oxydised than the tannins or catechins and are still monomolecular, crystalline and do not appear to form " Reds " easily.

The deepening of the colour of tanning materials and of extract powders observed on exposure to light is also probably caused by a further condensation and can be brought about in the absence of oxygen or air.

On the other hand, oxygen if present during polymerisation or condensation of tannin in extracts, may react with tannin, but will probably result in the formation of a different type of insoluble

29

derivatives. This conclusion can at least tentatively be drawn from the mauve or even blackish colouration such products attain under the influence of oxidising agents and which is sometimes observed in deposits of boilerwaters which for the purpose of de-oxidation have been treated with flavotannin extracts.

The conversion of the single catechin units into condensation products may perhaps be compared with a kind of resinification. Flavotannin extracts contain in general a whole series of condensation products, some extracts still contain the monomolecular units in their primary form. The highest condensation products when separated from the less condensed modifications, are quite insoluble and within the extract are kept in solution by a kind of colloidal peptisation partly due to the lower members of the series. This colloidal state can be disturbed by varying means, dilution, lowering of temperature, salting-out and other phsyical changes.

In a number of tanning materials of this class a yellow dyestuff of the anthoxanthin[139]) type is found which may be considered to be a glucoside of an oxidation product of the simple catechin unit usually forming the basis for the respective type of tannin. Sometimes it is not the glucoside or anthoxanthin, but the simple anthoxanthidine that is present. Depending on the number and position of the hydroxyl groups, these anthoxanthidines generally vary with the tannins in the respective material and as they are of crystalline nature they assist in interpreting and identifying the tannin. Their general structure includes the flavone complex :
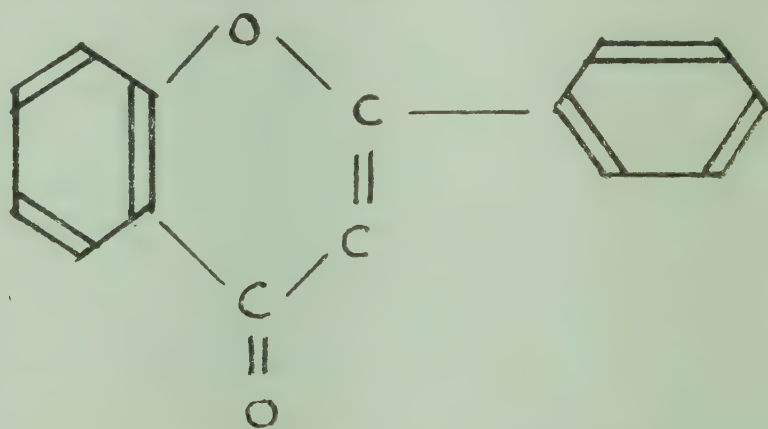
The phlobaphenes, as long as they are held in solution or are at least colloidally dispersed, play in the tanning process probably a part similar to that of the " bloom " during the tannage with gallo-tannins.

The various flavotannins although apparently based on only a few different catechins seem to vary a great deal in respect of the quantities and qualities of phlobaphenes or " insolubles." The reasons for these differences may perhaps have something to do with the difference in the character of the non-tanning constituents, and of the type of catechins from which the tannins are derived. Non-tanninsmaybe responsible for the relative reduction of insolubility on account of peptising faculties of sugar-like components or the solubi-lising influence of alkaline constituents of mineral matter present.

Some tannins contain a minute quantity of proteinic matter,[140] at least of nitrogenous compounds which also may exert a differentiating effect in the amounts of soluble tannin.

Differences in the acidity have also to be taken into consideration.

Varying numbers of hydroxyl groups in the simple building elements have probably an additional influence, in so far as for instance flavotannins based on the one hand on pyrogallol or at least partly on pyrogallol, and on the other hand, on phloroglucinol, are likely to be more soluble than such as are based on catechol and resorcinol respectively.

Among other factors which may possibly give rise to differences in the degree of polymerisation and condensation are climatic conditions and age of plant and perhaps the particular section of wood or bark in which the tannin has been deposited.

Catechins may be called all such substances as are derived from flavane or flavene which possess different numbers of phenolic hydroxyl groups. Several types of catechin have so far been isolated, or assumed to form the bases of the flavotannins. Some of them have already been synthesised.

The majority of catechins seem to contain phlorogucinol, whilst quebracho-catechin has resorcinol attached to the dihydropyrane complex.

Catechin itself and quebracho-catechin contain a catechol ring as second component, whilst casuarin has a pyrogallol component. Cyanomaclurin has resorcinol and one of the two so far hypothetical catechins in Robinia Pseudacacia may contain phenol, the other one pyrogallol.
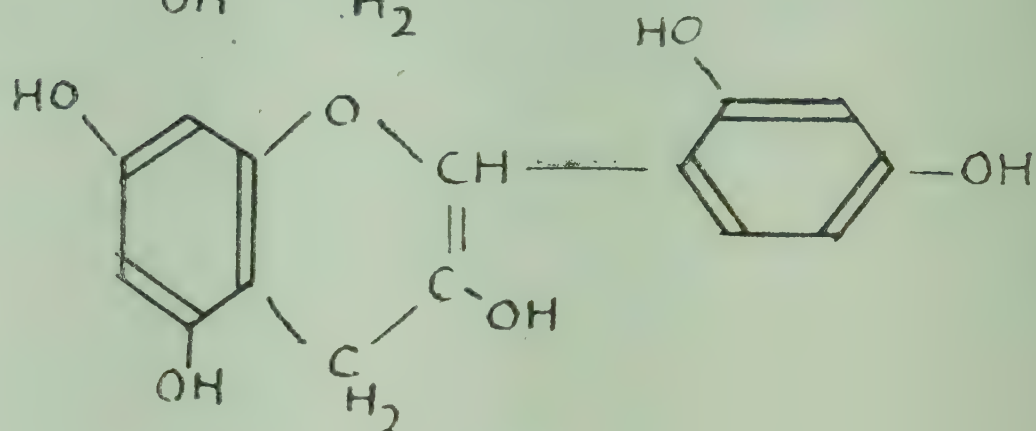
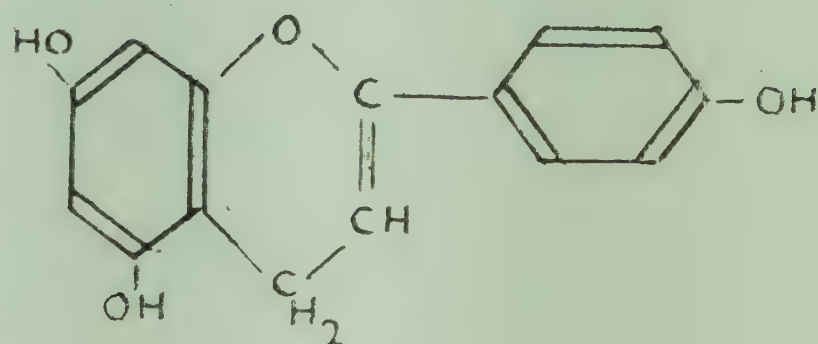These six types would thus be represented by the following formulae :

a). Catechin (par excellence).

b). Quebracho catechin
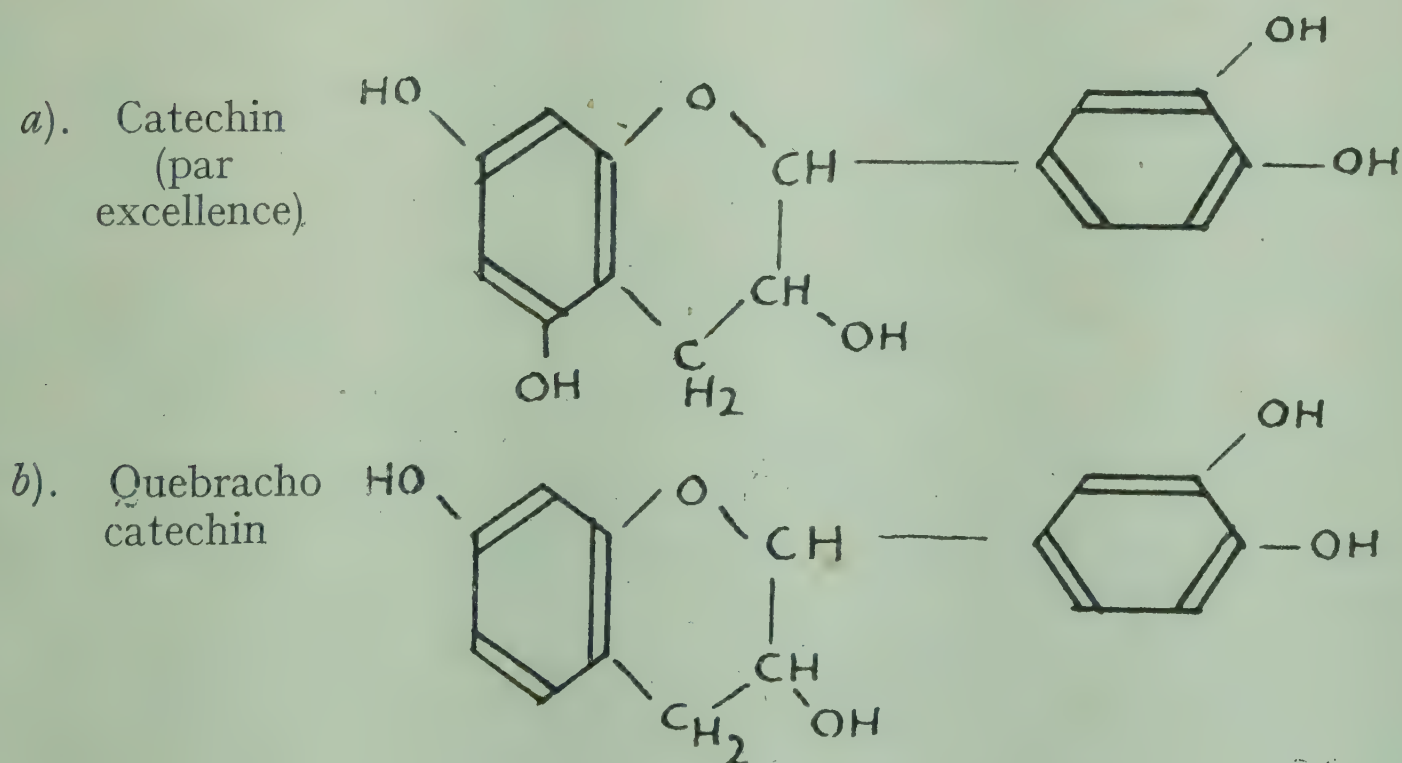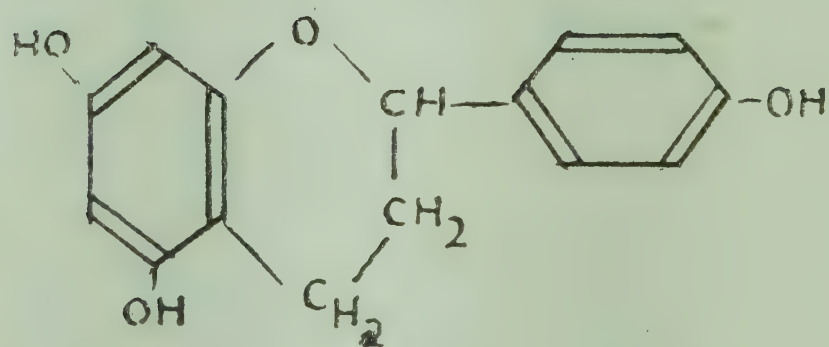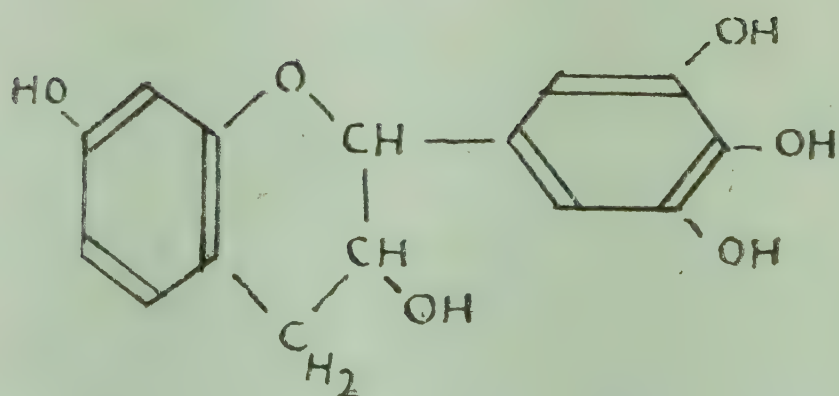
c). Casuarin
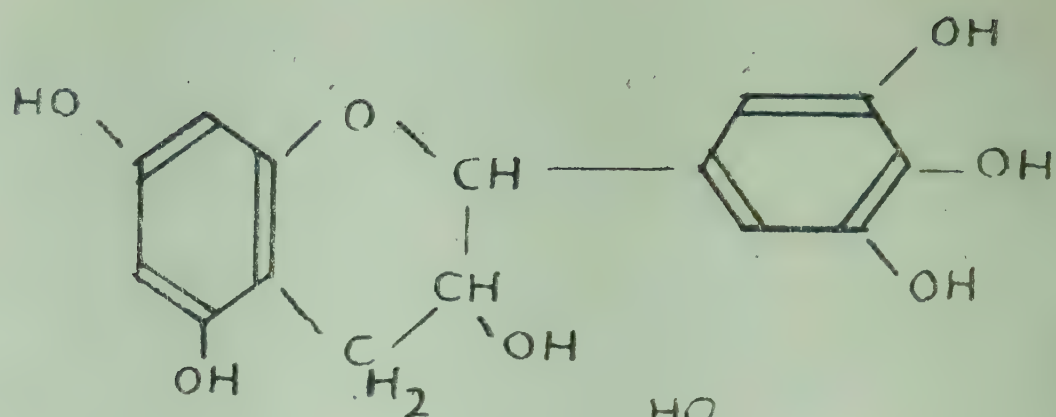
d). Cyanoma-
    clurin

e). Robinia
   catechins

or

and

32

In agreement with these formulae the products of decomposition obtained on direct heating and on treating with caustic alkali respectively are as follows :—

	Heating.	Fusion with alkali.
a).	Catechol	Phloroglucinol and protocatechuic acid.
b).	Catechol	Resorcinol and protocatechuic acid.
c).	Pyrogallol	Phloroglucinol and gallic acid.
d).	Resorcinol	Phloroglucinol and β-resorcyclic acid.
e).1).	Phenol	Phloroglucinol and parahydroxy-benzoic acid.
2).	Pyrogallol	Resorcinol and gallic acid.

Our understanding of the nature of flavotannins can probably be deepened if we are allowed to dwell a little on their probable formation in nature and consider them in connection with another natural product very frequently occurring in plants, i.e. the lignin.

According to K. Freudengerg, lignin is probably derived from sugar and it may be assumed with some degree of likelihood that the flavotannins have a related origin.

Both lignin and flavotannins contain an aliphatic chain consisting of three carbon atoms :
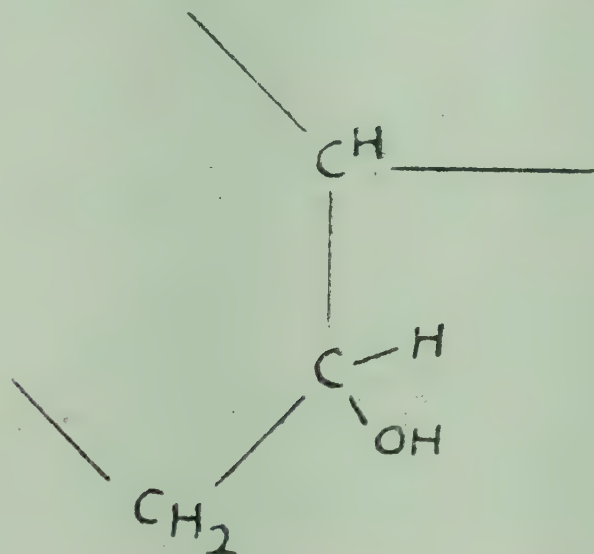
the formation of which may proceed as follows : At first an inter-position of a formaldehyde molecule has to be assumed between the carbon atoms No. 2 and No. 6 in glucose so that a ring closure is produced with six carbon atoms. The remaining carbon atom No. 1 now forming a side chain reacts thereupon with an acetaldehyde molecule or two further molecules of formaldehyde to form a propylated hydroxylated benzene complex.

Up to this point, the formation of lignin and flavane derivatives could proceed on similar lines. But from here on, the building up deviates in different directions.

Lignin which has to fulfil the purpose of reinforcing and protecting the cellulosic fibre chains—already to some extent water resistant—must also be rendered water resistant and less attackable. That aim is achieved by dehydration under formation of a heterocyclic ring including an oxygen bridge, by rendering

inactive some hydroxyl groups which otherwise would generate solubility, by forming methyl or methylene ethers with further molecules of formaldehyde and by polymerisation of this simple unit manifold to a large highly molecular complex.

This theory would express the fact that lignins in their simplest units possess a benzene ring, one phenolic methoxy group and one hydroxyl group in an aliphatic side chain of three carbon atoms which form a heterocyclic closure.

Primary lignin as existing when still in the plant, before postmortal con-
densation and
before chemical
attack, seems to
be based on this
schedule :

wherein the methoxy group may be in meta or in para position, the side chain may be straight or branched, the aliphatic hydroxyl group may be on carbon atoms 1 or 2, the 3-position as a primary one being unlikely.

A. M. Paleev[141]) states that primary lignin does not contain methoxyl, but that the latter increases in the lignin with concurrent decreases in the amount of carbohydrate containing methoxyl groups, which would indicate an original formation of methoxyl in carbohydrate and a subsequent gradual transfer to lignin.

In accordance with the fact that a small quantity of formaldehyde can be split off from lignin, a correspondingly small percentage of dioxymethylene groups must be assumed to be present in the molecule. That amounts to one dioxymethlene group for every twelve units. Apart from these units with dioxymethylene, a heterocyclic five- or six-ring must be assumed in each unit, which may, however, be formed in quite a number of ways. Such possibilities would for instance be shown by the following schedules :[142])
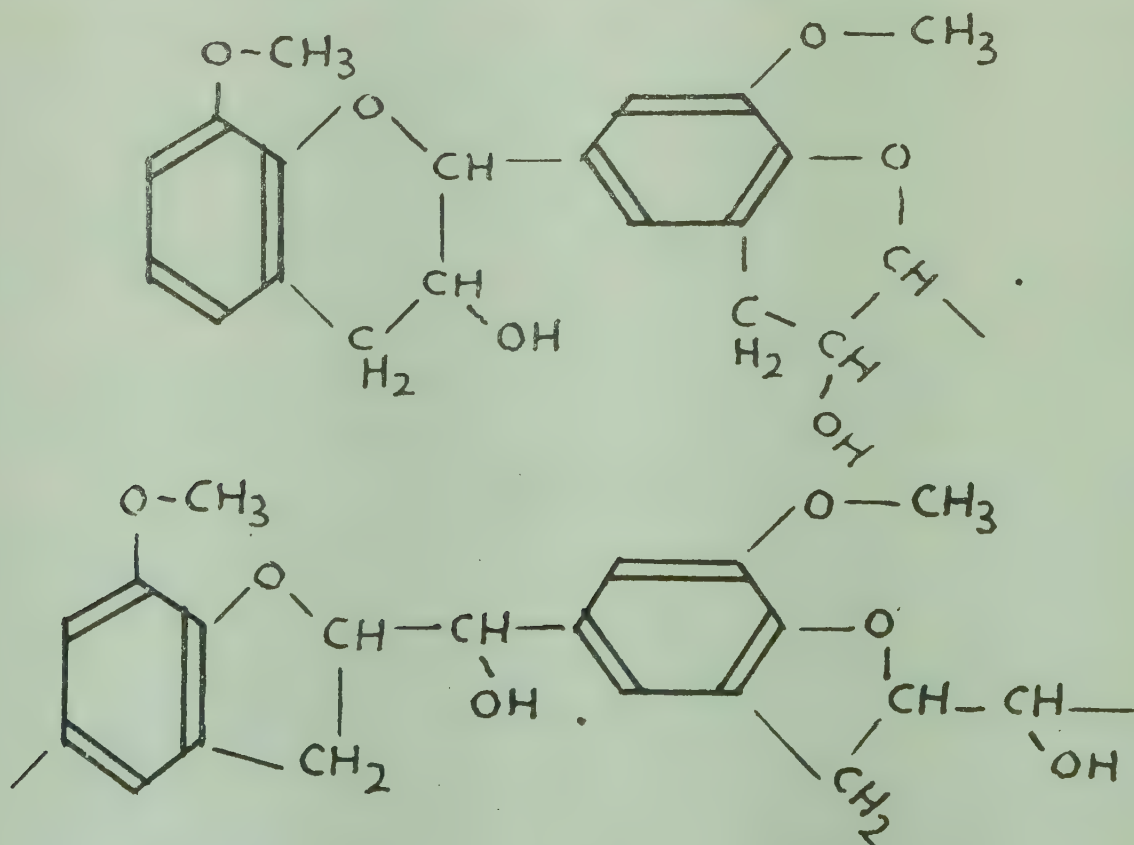
These two configurations show an interesting similarity to that of flavotannins and catechin.

Catechin   HO   O   OH   CH — OH   CH CH_2 OH   OH
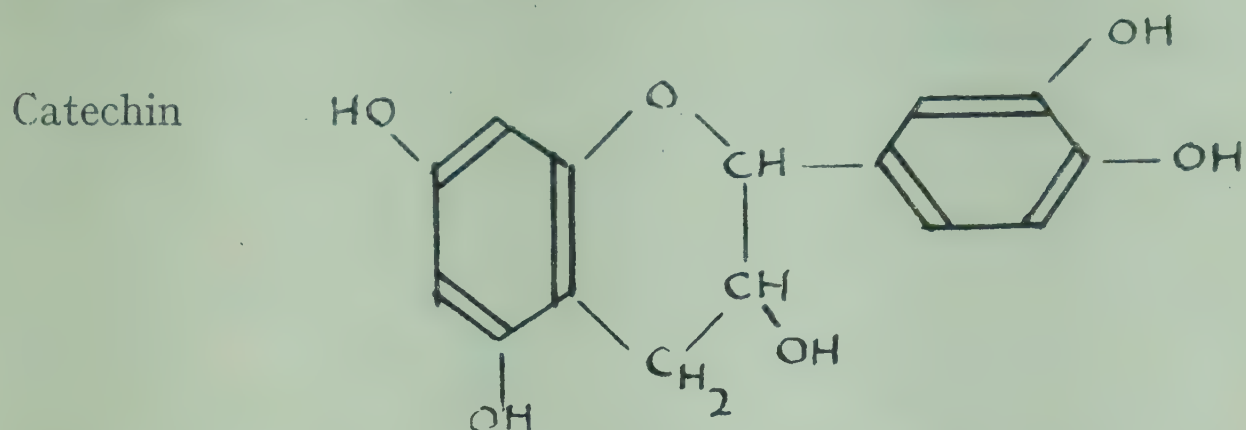
In the case of lignin we see either a benzodihydropyrane or a benzodihydrofurane nucleus, in catechin a benzodihydropyrane nucleus. Whilst catechin is a tetrahydroxyflavanol, the first of the two above schedules could be considered as a dimethoxy-flavanol, to the second benzene ring of which another dihydropyrane ring is attached.

Spruce lignin is probably exclusively derived from catechol, whilst beech wood lignin contains apparently a small quantity of pyrogallol derivatives. Beech wood lignin has a higher content of methoxy groups and beech wood tar contains dimethyl-pyrogallol.[143]

The main differences between lignin on the one hand and catechin on the other hand are as follows :—

1). Lignin has no free phenolic hydroxyl group, Catechin has a great many.
2). Lignin has the methoxy group in orthoposition to the pyrane oxygen bridge, whilst in catechin the phenolic hydroxyl groups in the benzopyrane nucleus are both in meta position to the pyrane oxygen bridge.
3). Lignin appears to be a polymerisation compound consisting of a multitude of either benzodihydropyrane or benzodihydro-furane or similarly built nuclei, whilst catechin possesses an additional benzene ring in the molecule, i.e. two aromatic rings for one pyrane ring, (lignin has only one aromatic ring for one pyrane ring).

The result is that primary lignin is an amorphous insoluble polymerised substance and may consist of simple units differing from each other and branching off in all three dimensions.

Catechins and the flavotannins derived therefrom in their lower stages of polymerisation are soluble compounds, the flavotannins themselves are amorphous polymerised substances which consist of equal simple units.

Lignin sulphonic acid, the principle of sulphite cellulose waste liquors obtained in pulping spruce wood, according to K. Freudenberg,[144] like primary lignin when still in the wood is not of uniform molecular weight, but consists of a mixture of polymer-homologues of up to very high molecular weights (of the order

35

10,000). The acid possesses one SO_3H group for every 3 to 4 units ($C_{10}H_{10}O_3$). This SO_3H group enters by splitting up the oxygen ring and by liberating a phenol group. Thus whilst there is one aliphatic hydroxyl group for approximately every complex of 10 carbon atoms, there is only one free phenolic hydroxyl for every 30 to 40 carbon atoms. The existant, though greatly limited degree of tanning capacity of lignin sulphonic acid is to be attributed to the high molecular weight and to the small number of free phenolic hydroxyl groups. A less highly sulphonated material might have a slightly better tanning capacity. The aliphatic part with the aliphatic hydroxyl group perhaps also reduces the affinity to hide substance. Briefly stated, the necessary polarity is mainly brought about by strong mineral acidity, not by phenolic hydrogen.

By chlorination and subsequent replacement of chlorine by hydroxyl groups (phenolic), O. A. Mueller claims to increase the tanning capacity of the sulpho-lignic acid.[145])

Synthetic tanning extracts, in common with lignin sulphonic acid, possess a high polarity due to a high ratio of sulphonic acid groups. The rule is here, however, that the more highly condensed the syntans are, the more they split off sulphuric acid again,[146]) so that with increasing molecular weight the ratio of SO_3H is reduced and the ratio of the aromatic hydroxyl groups increased. The better types of syntans are those that either have no sulphonic acid groups at all, but a comparatively high number of phenolic hydroxyl groups, concomitant with a considerable molecular weight or have the number of solubilising SO_3H groups strongly reduced by conversion of SO_3H groups in a terminal position into —SO_2— groups (Sulphone groups) in a central position.

Among artificial substances with tanning property containing no sulphonic acid groups are to be mentioned such as are made by condensation with formaldehyde, of polyhydric phenols, e.g. resorcinol, and two classes of compounds which lately have been made by A. Russell and coll.

A. Russell prepared several series of gallic acid esters and showed that simple esters of gallic acid with alcohols have no tanning property, but found that by esterification of polyhydric alcohols and particularly of sugars with several molecules of gallic acid, products could be obtained with good tanning property. Among the compounds which showed a fair tanning capacity were hexagallates of mannitol and sorbitol, whilst pentagallates of glucose and mannose and tetragallates of d-arabinose and a-methyl glucose possessed very good tanning capacity comparable with that of tannic acid (Chinese tannin). On the other hand, a pentagallate of fructose, although providing a good gelatin test and a blue-black colouration with iron alum, had no tanning property.[147])

The other group of compounds prepared by the same author comprises the various " Flavpinacols " obtained by condensation

of different aromatic hydroxyketones with various aromatic hydroxyaldehydes and reduction of the hydroxychalcones thereby produced. Some of these are dealt with in the chapters on Wattle and Hemlock. The products obtained are stated to be indistuinguishable (qualitatively) from natural tannins. A. Russsell maintains that quite a number of natural flavotannins are constituted in a similar way, i.e. as flavpinacols with hydroxyl groups in the 4-position in contradistinction from catechins which have the aliphatic hydroxyl group in the 3-position.[148])

Most of the above cited artificial tanning agents are derived from hydroxylated aromatic substances and possess phenolic hydroxyl groups. For the purpose of the conversion of an organic compound into a tannin it does, however, not seem to be an essential requisite for the original compound to possess phenolic hydroxyl groups or to be derived at all from a carbocyclic substance. On the one hand, condensed sulphonated napthalin and other aromatic hydrocarbons show a slight tanning property and on the other hand, more recently, some low polymerisation products of methylol urea and methylol melamine have been claimed to convert skins into leather. It appears as if the general unsaturated character of a cyclic compound, carbo- or heterocyclic, would render any negative polar substituent a potential leather producer.

THE PRINCIPAL COMMERCIALLY IMPORTANT FLAVOTANNINS.

They comprise the following different tanning materials:
    Gambier and Catechu or Burma Cutch.
    Quebracho.
    Tizerah.
    Urunday.
    Wattle.
    Mangrove.
    Spruce.
    Hemlock.
    Larch.
    Willow.
    Avaram.

GAMBIER AND CATECHU OR BURMA CUTCH.

Leaves and twigs of Uncaria Gambier (Hunt.) Roxb. a member of the family Rubiaceae, yield gambier extract or yellow catechu. East Indies, Malaya.

Wood of Acacia catechu (L.f.) Willd., a member of the family Leguminosae, yields cutch or dark catechu extract (called Burma Cutch). India, Burma, also in tropical Africa.

The two tanning materials are closely related. Both contain an appreciable quantity of crystalline catechin in various stereo-isomeric modifications, Gambier containing mainly d-catechin besides a small amount of d-epicatechin and Cutch containing varying quantities of l-epicatechin, l-catechin, dl-epicatechin and dl-catechin. The original modifications seem to be d-catechin and l-epicatechin, whilst the other variants are transformation products thereof.[149]

The percentage content of catechin varies in the extracts. During extraction from the plant material, some portion is converted into true tannin, whilst another part seems to be transformed into other modifications of catechin.

The same and similar catechins have been found in :
Chinese Rhubarb.
Guarana (Paullinia Cupana).
Mahogany wood and other plants.

The simple structural formula of the catechins in Gambier and Cutch is as follows (not considering the variations due to stereo-isomerism) :
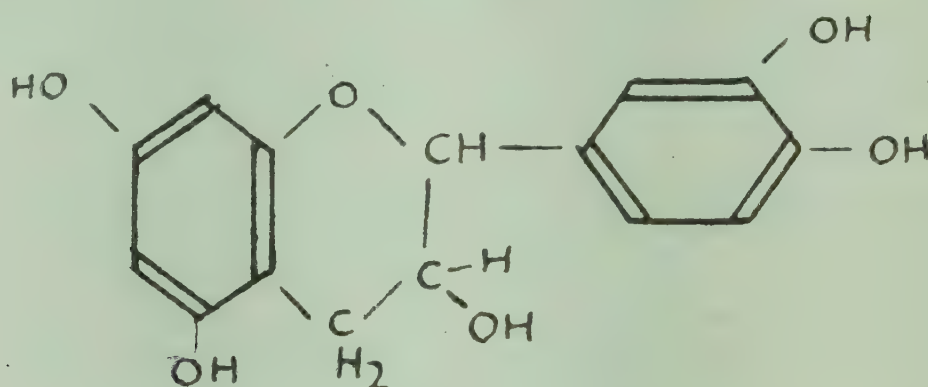
Catechin has no tanning properties and does not precipitate gelatine in dilute solutions, but it is stated[150] to be absorbed by hide in which it is gradually converted into tannin. Treatment with enzymes, acids, alkali with and without atmospheric oxygen converts it even in aqueous solution quickly into genuine amorphous tannins which precipitate gelatine.[151] Both the monomer and the polymers condense with formaldehyde to insoluble bodies.

In gambier and in cutch extracts a small quantity of a yellow dyestuff accompanies the tannin, that is the dyestuff quercitrin, a rhamnose-glucoside of quercetin which is a direct relative to catechin and has the following formula :

Quercetin.

= tetrahy-droxy-flavonol
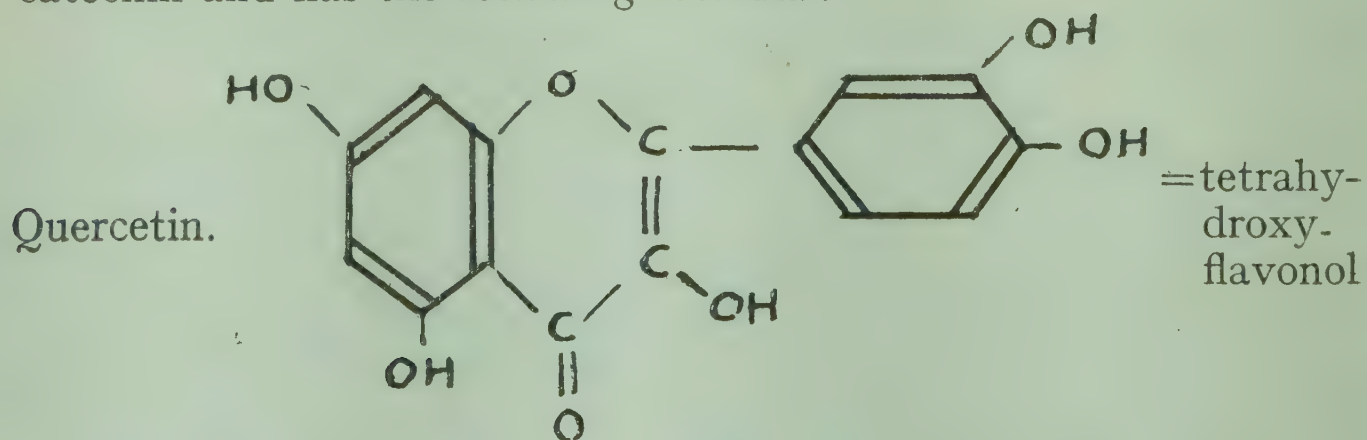
Willstätter and Mallison[152]) succeeded in reducing Quercetin by means of Magnesium and Hydrochloric acid to Cyanidine chloride and Freudenberg[153]) could reduce Cyanidine chloride to the dl-epicatechin by catalytic hydrogenation with Platinum black. Finally, Freudenberg showed that Quercetin (in form of the pentamethyl ether) can also be directly converted into epicatechin.[154])

The fission products obtained with caustic are protocatechuic acid, phloroglucinol and acetic acid.[155]) Both catechin and the actual tannin yield these products. The tannins in Gambier and and Cutch have obviously their origin in the polymerisation, condensation and dehydration of several single catechin units to a variety of chains of different lengths and can also be produced at will from the catechin, e.g. by heating.

Cotton wool impregnated both with normal and with alkalised analytical solution of Gambier extract, (brand "Plantation Gambier") shows in screened ultra-violet light an indistinct dull yellow fluorescence, whilst Burma Cutch, (brand "Pegu Cutch") yields a distinct, but not very bright yellow and an indistinct dull mauve fluorescence respectively.

Quebracho.

Wood of Schinopsis Lorentzii (Griseb.) Engl. (Quebrachia Lorentzii Griseb.) and other species of the family Anacardiaceae. Possibly trees belonging to other families may yield the same or a similar type of extract. Chiefly occurring in Argentina and Paraguay.

The tannin is contained almost exclusively in the heart wood. The sap wood is stated to contain a small percentage only of tannin, the aqueous infusion of which sometimes gives a blue colouration with ferric salts and may therefore contain pyrogallol derivatives.

G. A. Fester and F. Gargatagli[156]) found 2% of gallic acid in the leaves of Quebracho colorado, but only traces of protocatechuic acid; they concluded that the leaves do not contain tannin.

G. A. Fester[157]) believed that there are two botanically independent Quebracho trees, one of which, from gallic acid produces the gallotannin of the white wood, and another, from one or various catechins of the Freudenberg formula, the "catechotannin" of the coloured wood.

Perkin and Gunnel[158]) found small quantities of ellagic acid and of gallic acid in Quebracho wood and may for their experiments perhaps have used wood including sap wood. They also ascertained the presence of the anthoxanthin Fustin which is the rhamnoside

of the anthoxanthidine Fisetin of the following structure:

Fisetin

Trihydroxy-flavonol.
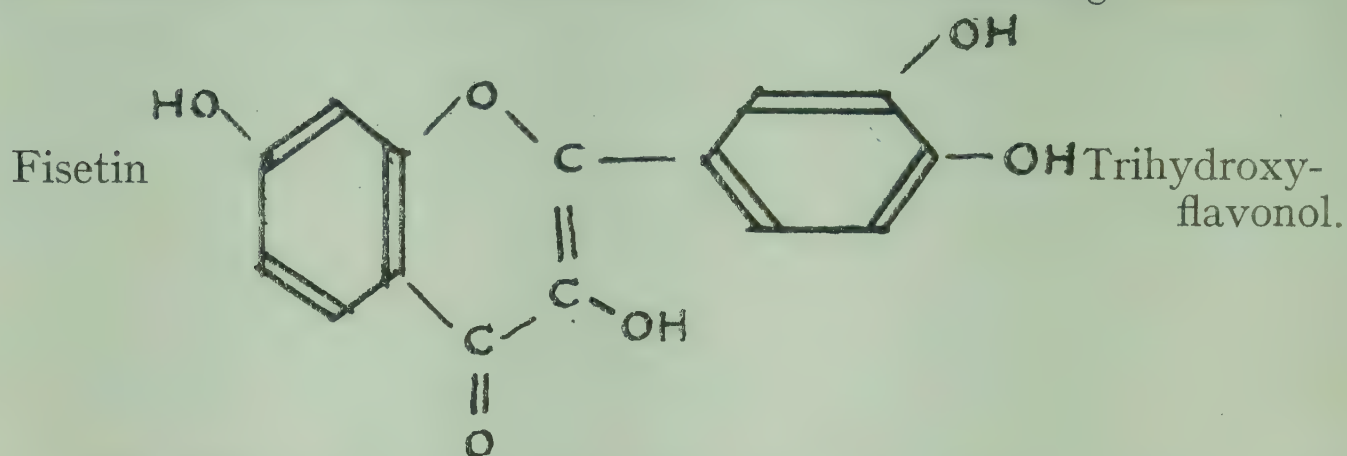
M. Nierenstein held the view that Querbracho tannin is a mixture of at least two tannins, yielding phloroglucinol and protocatechuic acid on the one hand and vanillic acid, hydroquinone and resorcinol on the other hand.[159]

The catechin which would correspond to fisetin :—

= Trihydroxyflavanol
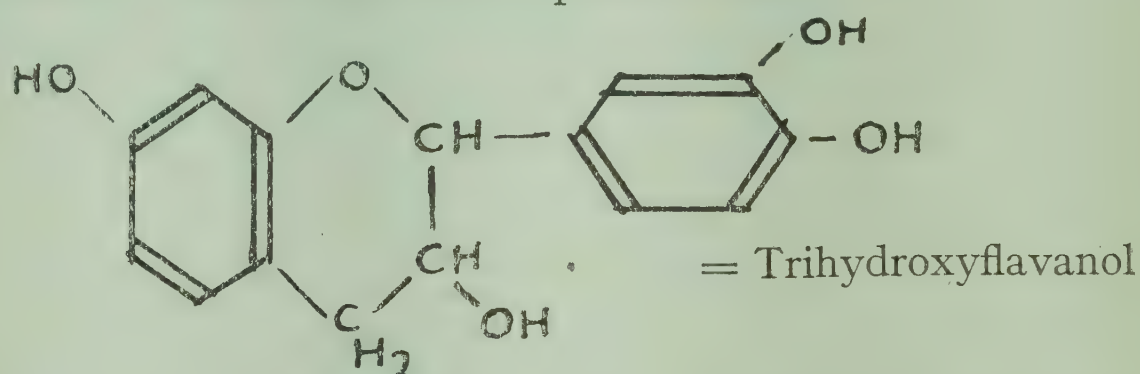
has not been isolated and is probably not present in Quebracho extract in its monomolecular form, but only in condensed form as, tannin. It has been artificially produced by K. Freudenberg[160] by catalytic reduction of the corresponding anthocyanidin chloride viz. fisetinidin chloride.


+2H₂

+HCl

40
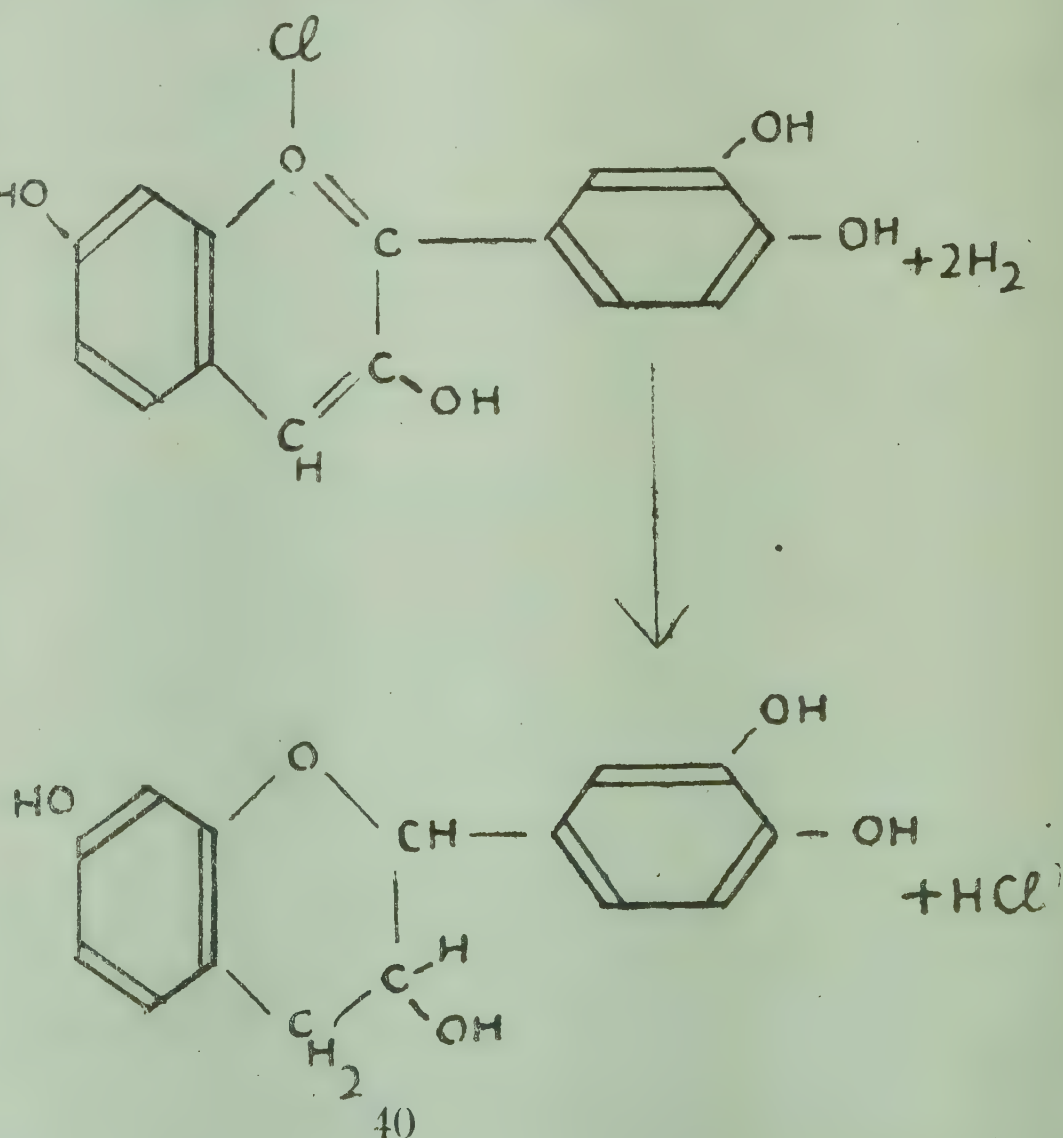
The respective catechin thereby obtained was dl-epiquebracho catechin. It resembled very strongly gambier catechin and on treatment with acids condensed very easily to amorphous tannins.
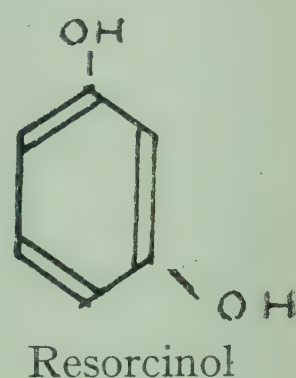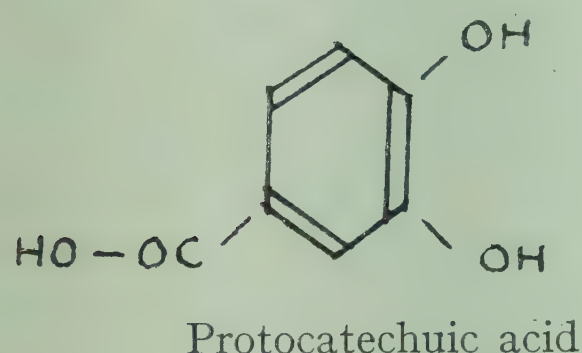
The above structure of a trihydroxyflavanol as that of the single quebracho catechin unit seems to be firmly established.

The following decomposition products of Quebracho have been obtained:

on dry distillation: catechol
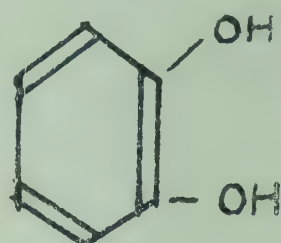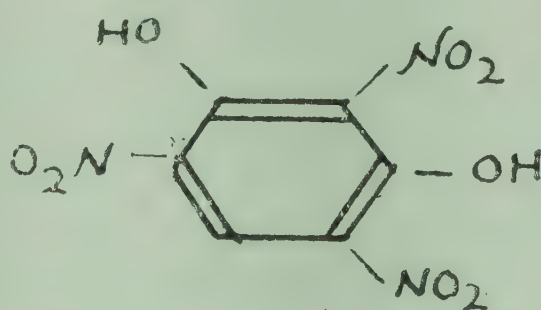
on fusion with caustic: protocatechuic acid, acetic acid and resorcinol

Protocatechuic acid   Resorcinol

Some earlier authors[161]) believed to have obtained phloroglucinol which observation according to more recent work must have been based on misinterpretation.

On treatment with nitric acid :[162]) styphnic acid = trinitroresorcinol

on fusion with phthalic anhydride : [163]) fluorescein

41
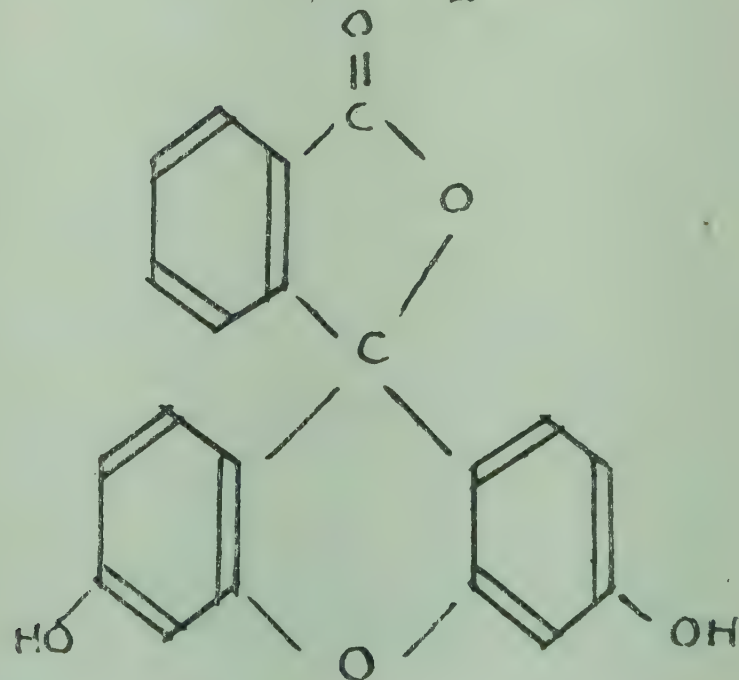
All these reactions confirm the presence of a catechol and a resorcinol nucleus.

With regard to the fluorescein reaction with phthalic anhydride it is interesting to note that the reaction occurs with the extract, but not with the wood. Quebracho-tanned leather gives the same reaction as extract. The different behaviour of Quebracho wood from Quebracho extract may perhaps be interpreted as indicating that the tannin in the wood is contained in a form different from that in the extract and that the tannin during extraction undergoes some kind of transformation.[164])

This argument might perhaps also be supported by observations made during the manufacture of plastics from thermosetting moulding powders based on Quebracho tannin, viz., the considerably greater ease of moulding with some resin-forming components, e.g. phenol and cyclohexanone in the presence of Quebracho wood as compared with mixtures of Quebracho extract and wood flour.

It was found that Quebracho tannin in the presence of aldehydes, for instance paraformaldehyde, exerts a catalytic influence on resin-forming components such as aniline, phenol, cyclohexanone and amides and not only converts them into the initial fusible and soluble resins but in one single operation, immediately into the infusible and insoluble final condensation products. This property is apparently shared by other catechins which possess a resorcinol or a phloroglucinol nucleus and was therefore called the " catechin effect." Experiments conducted with several different mono- and polyhydric phenols showed that this effect is attributable to phenols which have two hydroxyl groups in meta position as it is the case for instance in resorcinol.

Molecular weight determinations carried out with electrodialised solutions by G. W. Douglas and F. E. Humphreys make it probable that the average molecular weight of Quebracho tannin is above 2,500.[165])

Quebracho extract according to the Official method of Tannin Analysis contains approximately one tenth of the total tannin in insoluble form, whilst the other nine tenths are soluble in cold water. Whilst this observation refers to a certain very weak concentration at a standard temperature of 18°C, the quantities of sediments deposited in other conditions depend completely on concentration and temperature. It is possible to separate the aqueous extract solutions into different fractions of varying solubility. Electrolytes, e.g. salts or acids, may be used during such fractionation and increase the quantities of sediments.

Normal Quebracho extract which is only difficultly soluble in cold water, by a treatment with sulphites or bisulphites at elevated temperatures with or without pressure, is rendered easily soluble in cold water.[166]) The usual " solubilisation " is carried out with approximately 6% to 7% sodium bisulphite calculated on solid extract with about 80% total solids. The fractionated sediments require

more and more bisulphite in accordance with the ease with which they have been thrown out of the colloidal solution and this in its turn must be considered to be a sign of a higher state of polymerisation and molecular weight.

It is perhaps reasonable to argue that the ingredients (in Quebracho extract) of the lowest solubility are hardly susceptible to bisulphitation and that during the usual treatment of extract with bisulphite they are not affected at all but are kept in solution by the increased peptising (i.e. particle reducing) action of the bisulphited portion even in dilute soluton. These soluble phlobaphenes resemble in a certain measure condensation products of Quebracho extract obtained by treatment with formaldehyde, which are in general not capable of solubilisation with bisulphite.

The tannin in bisulphited extracts, on gradual condensation with formaldehyde undergoes a gradual change from soluble tannin through soluble non-tannin to insoluble non-tannin. Up to a ratio of 1% CH_2O (100%) calculated on extract with approximately 88% total solids, no noticeable reduction of tannin can be observed, whilst at ratios of above 1% CH_2O (100%) more and more tannin turns into non-tannin, until at a ratio of 3% CH_2O (100) no tannin is left. From 1% to 2% the solubility remains the same and is actually slightly improved. The tannin which then to a great extent has been converted into soluble non-tannin is found to have turned into a highly gelatinous solid substance even more soluble than the original liquid extract which itself may deposit a minor quantity of sediment. Above 2% CH_2O (100%), the solubility is rapidly reduced until at 3% the tannin has been rendered completely insoluble. Further increase of the ratio of CH_2O increases the molecular size, whilst the absorptive power of the insoluble materials towards water and the cations in water which power is particularly remarkable in insoluble condensation products made with highly bisulphited extracts is reduced.

The base exchange capacity of aldehyde condensation products of untreated flavotannin extracts is rather moderate, but increases with bisulphitation of the untreated extract. The manufacture of highly efficacious cation exchange materials based on flavotannins which hitherto has been carried out in two stages and which prior to condensation necessitated a strong bisulphitation requiring heating for periods of several hours, is greatly facilitated by a simultaneous heat treatment of the untreated extract with sulphite and an amount of formaldehyde more than equivalent to the quantity of sulphite employed. Such a method requires a few minutes only.

Tanning with extracts, bisulphited and treated with small quantities of formaldehyde (i.e. up to 2%), is greatly inhibited beacuse although the extracts are perfectly soluble, the smallest particles are probably the most easily condensed and even the

43

slight condensation has increased their size to such an extent as to render them incapable of penetration.

In the case of tannins with lower original particle size, such a treatment as here described may perhaps be found useful in the improvement of the tanning property.

Further support for the formulation of Quebracho catechin as a trihydroxyflavanol is lent by work carried out by M. Bergmann and G. Pojarlieff[167] on the bisulphitation of Quebracho extract. They found, that only one half of the bisulphite entering the tannin molecule was easy to split off by alkali, which result was compatible with results formerly obtained in the bisulphitation of resorcinol by H. Bucherer[168] and W. Fuchs,[169] and that as catechol itself was proved to be indifferent towards bisulphite—the whole of the bisulphite was assumed to have entered the resorcinol portion.

Some work on the action of bisulphite on Quebracho tannins and non-tannins has been carried out by Turley and collaborators[170] who differentiate between three types of bisulphitation products

a). true sulphonic acids on carbon atoms free from OH groups
b). hydroxyl sulphonic acids on carbon atoms holding OH groups
c). sulphurous acid esters on the 3-OH group in the dihydropyrane ring.

A somewhat different type of solubilisation of difficult soluble tanning extracts (for instance Quebracho) may be achieved by heating for a short period the aqueous extract solutions with an additive compound of sulphite and formaldehyde produced by a simple admixture of sulphite and formaldehyde solutions in equimolecular proportions.

During this reaction methylene-sulphonic acid groups ($-CH_2-SO_3Na$) are introduced accompanied by a weight increase of the affected tannin molecule by about 40% and under formation of free sodium hydroxide. As before the solution is employed for tanning, the latter requires neutralisation, a fair amount of inorganic salt is formed which in addition to the modification of the character of the tannin has a definite influence on the tanning qualities.

The treatment seems to require considerably less time than a normal bisulphitation : it is for instance possible to solubilise ordinary Quebracho extract in one hour only or even less, if it is treated with as much formaldehyde-sulphite compound as is required for the whole of the tannin present.

Other types of soluble Quebracho extract have been prepared by simple fractionation under varying conditions of concentration, temperature and acidity.

A. Redlich and coll.[171] manufactured soluble Quebracho extract by dissolution of the sediment deposited during fractionation, with small quantities of alkali and addition of a certain portion of this solution to the supernatent liquors, until flocculation occurred.

44

During fundamental research, e.g. in trying to establish the nature of various decomposition products of flavotannins the methods usually employed with tannins as given by nature or after purification or with phlobaphenes produced on acid treatment, should be extended to include bisulphited extracts, insoluble condensation products of normal and bisulphited extracts, formaldehyde-sulphite-compound treated extracts and such of the latter type as by use of an excess of aldehyde have been rendered insoluble.

The decomposition products would probably disclose interesting facts, for instance the position in the original molecule where the chemical reaction (bisulphitation, condensation) has taken place.

The following points among others, seem still to require clarification.

Degree of condensation or polymerisation of various fractions of phlobaphenes. (molecular weights).

Manner in which several catechin units are linked together and particularly in relation to the aliphatic OH groups.

Determination of the extent of polymerisation which brings about insoluble products.

Determination of conditions of extraction leading to less insoluble extracts or, what is the same, to more soluble commercial products.

It would also be interesting to determine the number per tannin unit, of active hydroxyl groups contained in various tannin fractions obtained from Quebracho extract at different temperatures. These figures would probably show a decrease in relation to the molecular weight of the tannins soluble at the respective temperatures and throw light on the inactivation of polar groups caused by polymerisation or condensation.

Powders of Quebracho wood and extract and Quebracho tanned leathers when kept in direct light, turn deeper in colour, red or brown. This must be considered to be due to formation of products of higher degrees of polymerisation or condensation. A similar phenomenon can be observed when solubilised extract solutions are gradually more and more strongly acidified. It has been noticed that below a pH of about 3, at least the deposit turned quite noticeably a fiery colour.

Oxidation does not seem to play a part in this change of colour as when extracts and leathers were treated with real oxidising agents the colour turned not brown but a blackish nuance of blue, sometimes almost mauve. Nitric acid in the cold did not react in this way as it apparently merely acted as an acidifying agent.

It would be useful to determine the conditions necessary for the production of more light-resistant leathers.

The cause of this faulty behaviour of the Quebracho tannin may perhaps also lie in the aliphatic hydroxyl group in the dihydropyrane ring. If that is true, a remedy could perhaps be found in blocking this group by means which should be compatible with commercial necessities and with solubility.

Further studies should be made regarding the action of bisulphite on the tannin, the nature of the non-tannins and the action of the bisulphite on the latter.

Another point worth studying is the change of colouration with iron to blue and the loss in capacity of forming insoluble aldehyde-acid precipitates in very highly bisulphited Quebracho extracts.[172]

It may also be of interest, at least of scientific interest, to investigate the possibility of converting some of the constituents of Quebracho sap-wood into tannins. Because of the close neighbour-hood of the greyish sapwood to the deeply coloured heartwood and because of the probability that the tannins are derived from ingredients either at first produced in, or migrating through, the sapwood before the tannins are deposited in their final form, some simple chemical (biochemical) reaction may be responsible for that change. A preliminary tentative experiment carried out by the writer with this change in view was unsuccessful.

In addition attempts seem to be worth while at breaking up the Quebracho tannin complex, at least the higher insolubles into smaller, possibly more soluble complexes by progressive treatment with alkali or other means at various concentrations and temperatures, keeping in mind that the end effect with the highest concentrations and at the highest temperatures is the total destruction and dissolution into resorcinol, acetic acid and protocatechuic acid.

Theoretically, one should think, there must be an intermediate stage or range of conditions, which would facilitate the loosening of the bonds existing between the single units and which would result in splitting up the large complexes into smaller units, unless of course the condensing links are stronger and more durable than the bonds in the original units.

In this connection, it should be explained why Quebracho extract liquors on heating for prolonged periods without or with alkali after exact neutralisation of the alkali employed turn more acid than before treatment and why in the case of heating with alkali the solubility is increased up to a certain ratio of alkalinity whilst beyond this ratio the solubility decreases again below the solubility of the original extract.

The increase in acidity which was found to be dependent on temperature, pressure, duration of treatment and concentration of extract, may perhaps be explained by partial splitting off of acetic acid from the dihydropyrane ring or by reactivation of free phenolic hydroxyl groups caused by opening up the tannin complex.

T. D. Braunschweig[173] expresses the hypothesis that " hidden acid groups " are hydrolised by the alkali in a way similar to the deolation of basic chromium salts by acid. He finds the degree of depolymerisation depends on a) time of boiling, b) concentration of alkali and c) kind of alkali.

In a later report, T. D. Braunschweig[174] makes an attempt at explaining the mechanism of bisulphitation on the basis of Turley's[170]

work and his own olation hypothesis.[173]) Through the formation of hydroxy- and of true sulphonic acids—by way of addition of the elements of bisulphite on double bonds—the aromatic character of the resorcinol nucleus in quebracho tannin is greatly altered under simultaneous reduction of the polarity of the formerly phenolic hydroxyl groups and of the tanning capacity.

It has, however, to be kept in mind that the quantity of bisulphite actually used in practice for satisfactory solubilisation is seldom more than 7% of (100%) NaHSO₃ calculated on the weight of quebracho extract with 80% total solids or 8.75% on oven-dry extract. At a purity figure of 87 to 90, this would amount to about 10% on the total tannin or to about 0.365 molecules of bisulphite only on one quebracho catechin unit, whilst the simultaneous introduction of all three types of bisulphitation groups (sulphite esters, hydroxy sulphonic acids and true sulphonic acids) would require three molecules of bisulphite. On the average therefore only a comparatively small number of catechin units can be simultaneously affected by all three reactions.

It is hard to visualise how the esterification of the aliphatic hydroxyl groups should influence the tanning capacity which therefore can only be reduced by the two other reactions. These, however, are stated not to take place until after the formation of the sulphite esters.

In view of the comparatively small quantity of bisulphite commercially employed, only a very small amount of bisulphite can therefore be engaged in those two reactions, and it appears thus to be necessary to revise the present theory of the correlation between reduction of tanning property and chemical reaction and perhaps to attribute a greater share to the physical phenomena accompanying the solubilisation.

Quebracho extracts after heating with acid and subsequent exact neutralisation of the acid employed, were found to have a higher pH than before treatment. This phenomenon is attributed to blocking and inactivation during the polymerisation, of acidity generating phenolic hydroxyl groups.

Since Quebracho sediments fractionated from untreated extract solutions show a lower pH than do the original solutions from which they have been deposited, it may be assumed that polymerisation is at first accompanied by an increase of acidity but from a certain point on, particularly under the influence of acids, acidic phenolic hydroxyl groups are inactivated, or that perhaps the products as formed in the plant or by mild treatment are of a type different from the products as formed by acids : that would mean that the former have perhaps a more open character and would be more of the polymerised type, whilst the latter would be more of the condensed type.

Ultra-violet light produces a brilliant yellow fluorescence on cotton wool soaked in normal Quebracho solutions and then washed, whilst a dull yellow fluorescence is shown, when the tanning liquor

has been rendered alkaline prior to the cotton wool being immersed. Aqueous infusions of Quebracho sapwood show almost the same fluorescence as infusions of Quebracho heartwood, only slightly less intense. This fact must indicate that both portions of the wood have some ingredient or ingredients in common.

The fluorescence is probably to be attributed to the dyestuff (fisetin) present in Quebracho wood and extract.[175] Fisetin has obviously some strong affinity to cotton fibre in neutral or acid solution, whilst in alkaline solution this affinity is greatly reduced but not quite obliterated.

The fluorescence is most likely due to the presence of the benzopyrone nucleus, as seems to be proved by the isolation and identification by R. J. Best, of scopoletin (7-hydroxy-6-methoxy-1, 2-benzopyrone) as the source of fluorescence in some inocculated tobacco plants.[176]

An old sample of bisulphited Quebracho extract was found by the writer to have lost its characteristic Quebracho fluorescence almost completely in so far as in normal neutral solution the fluorescence colour was white with a slight yellow tinge only, whilst the alkalised solution yielded no particular fluorescence but for the fluorescence of cotton wool, viz. dull mauve. Possibly the anthoxanthidine had been gradually reduced and its structure with the conjugated double bonds was broken up. In contradistinction from that old sample of solid bisuphited extract, recent manufacture shows a brilliance of fluorescence which is identical with that of untreated Quebracho extract.

The cause of this change or fading of fluorescence in bisulphited extracts with the age should be investigated. No such change was noticed by the writer in ordinary untreated Quebracho extract that had been in storage for over 40 years.[177]

The tree called Quebracho blanco the botanical name of which is Aspidosperma Quebracho blanco Schlecht. and which belongs to the family Apocynaceae, does not contain any appreciable amount of tannin in wood (stated to be about 3%) or in bark (about 4%); but the leaves have been said to contain up to 27% tannin.[178]

Recent samples analysed by the Official method, were found to contain only 1.0% in wood, 0.9% in bark and 4.0% in leaves. The classification of the tannin was difficult, particularly due to the fact that the gelatine effect was very weak and the colour reactions were non-characteristic. Based on the comparatively high pH-values of the respective aqueous infusions, the assumption was made that the tannin might perhaps partly be combined with alkaloids.

Cotton wool impregnated with aqueous infusions and inspected in screened ultra-violet light, exhibited a blue to violet fluorescence.

Tizerah.

Wood and roots of Rhus pentaphylla Desf. of the family Anacardiaceae. North Africa, Canaries and Sicily. Not much is

known about Tizerah tannin besides the fact that it resembles Quebracho extract very closely both in chemical properties and tanning quality. The main difference of the two tannins is the deeper colour of Tizerah and the fact that it had been proved difficult to reduce this colour to a satisfactory degree. The best results obtained by the writer in this respect were achieved in a simultaneous decolourisation with zinc dust and bisulphite and subsequent acidification to normal pH.

Ultra-violet light produces a dull mauve fluorescence on cotton wool soaked with alkaline Tizerah infusions and washed with water, in the case of Quebracho a dull yellow fluorescence is shown, whilst with the untreated aqueous infusions of both Tizerah and Quebracho, cotton wool soaked and washed exhibits a brilliant yellow fluorescence.

Untreated Tizerah extract contains approximately the same ratio of insolubles as does Quebracho extract ; these insolubles are phlobaphenes and will most probably have been formed in a similar manner to those in Quebracho. But apparently very little has been published on this matter in respect of Tizerah. Contrary to statements in literature,[179] Tizerah extracts lend themselves to solubilisation by means of bisulphitation.

It seems to be interesting to ascertain the decomposition products of Tizerah, so as to be able to form a picture of the structure of the tannin ; the nature of any dyestuff that might accompany the tannin would also be interesting to learn (perhaps fisetin).

The few experiments made in these laboratories with moulding powders based on Tizerah wood showed no difference between Tizerah and Quebracho and seemed to support the theory that the two tannins are either identical or very similar to each other.

Urunday.

Among the various trees called Urunday, for the purpose of tannin extraction, the wood of Urunday pardo (Astronium Balansae Engl.) of the family Anacardiaceae seems to be the only one of importance. South America. The tannin content seems to vary a great deal, between 6% and 14% or even more.

Urunday extract both untreated and bisulphited possesses a very intense colour which distinguishes it from Quebracho for instance.

There does not appear to be known anything about the chemical nature of Urunday tannin besides the fact that this tannin belongs to the group of flavotannins. The deep colour may mislead to the assumption that the tannin is highly polymerised or condensed, more than Quebracho. Urunday extracts, however, seem to be hardly less soluble than Quebracho extracts and the condensation with aldehydes proceeds with the same ease as with Quebracho. On the other hand, in making moulded products with plastic powders based on Urunday wood we encountered peculiar difficulties which at first let the

writer assume that the tannin in the wood was precondensed in a certain direction so that the polarity and catalytic reactivity of the resorcinol ring—if Urunday should be found to contain one—is greatly reduced. This result would also be in agreement with the low acidity or high pH of the aqueous infusions. Some hydroxyl groups are perhaps blocked, viz. methylated. In general, however, there are probably very few flavotannins that have methoxy groups. Perhaps it is the manner of polymerisation in which Urunday tannin is built up—possibly different from that of Quebracho—that is responsible for the lower catalytic influence of the resorcinol ring.

The fluorescence of Urunday tannin solutions is almost the same as that of Tizerah tannin solutions. Cotton wool soaked with Urunday solution and washed, exhibits a brilliant yellow light, whilst an alkalised Urunday solution on cotton wool, after washing, shows a dull mauve, i.e. the fluorescence colour of untreated cotton wool itself. If it is the fisetin that causes the yellow fluorescence in Quebracho, Tizerah and Urunday, it is difficult to understand why after alkalisation Urunday and Tizerah behave differently from Quebracho.

Some Urunday extracts on the market are probably mixtures with other tanning extracts, e.g. with extracts from the wood of Guayacan Itin = Caesalpinia melanocarpa. The bluish white fluorescence of cotton wool treated with such extract mixtures proves the presence of other materials.

Urunday tannin requires a thorough chemical investigation both for the sake of obtaining an insight into its constitution and for the purpose of finding means of converting it into a useful tanning material.

Also ascertainment of chemical nature of accompanying anthoxanthidine dyestuffs (if any) would assist in getting at the structure of Urunday tannin.

Wattle.

Bark of several species and varieties of the genus Acacia of the family Leguminosae, in particular of Black Wattle—Acacia mollissima Willd.—a native of Australia, but extensively cultivated in South and East Africa and other parts. On the continent of Europe, flower, bark and extract are known as " Mimosa," although this latter name is botanically reserved for a different genus of the family Leguminosae. In the United States of America too, the black Wattle is often called " Mimosa."

The tannin of Wattle bark belongs decidedly to the flavotannin class, but possesses a few peculiar features of its own ; the majority of flavotannins contain a comparatively great percentage of " insolubles " or phlobaphenes which from concentrated solutions are released and precipitated on dilution and/or cooling so as to form sludgy deposits containing up to 50% of the total solids present ;

50

Wattle bark extracts however, remain more or less clear, depositing only a small, almost insignificant portion of sediment.

The second phenomenon which has so far been puzzling is the faintly bluish colouration of the aqueous solutions of Wattle extract obtained when treated with iron alum[180] (shared only by malett bark infusions and a few other flavotannins) whilst the other flavotannins give a green colouration.

These two observations the writer has always thought to be indicative of products of a higher content of solubilising hydroxyl groups, particularly of the presence of a pyrogallol ring instead of a catechol ring in the flavane structure. This would involve the existence of a third type of catechin (in addition to the types of Gambier-catechin and Quebracho-catechin), viz. :

I.

or

II.
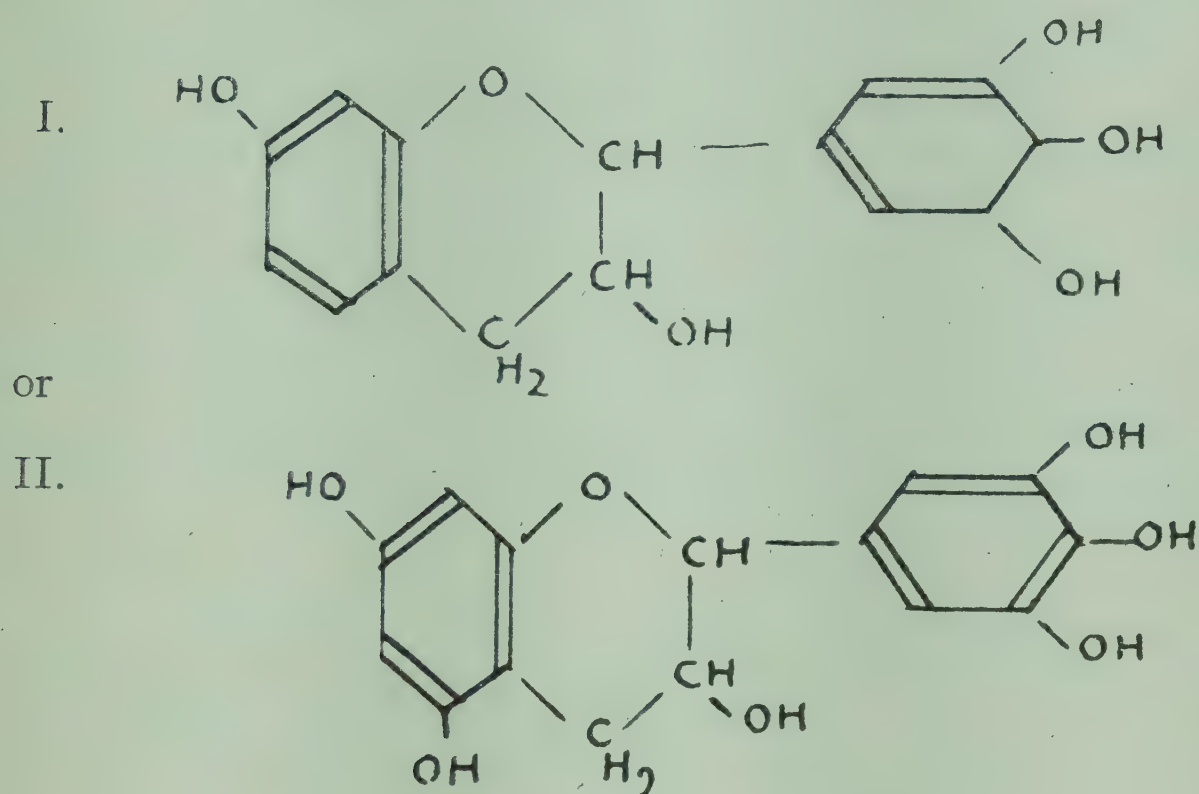
Actually a monomolecular catechin of the type II has been discovered and isolated in the bark of Casuarina equisetifolia = Filao of India and Madagascar by Yasugosi Osima[181] who called it " Casuarin." About eight years ago J. H. Corbett,[182] on oxidation of methylated Wattle bark tannin, identified trimethylgallic acid in addition to veratric acid which correspond to gallic acid and protocatechuic acid respectively.

Gallic acid

Protocatechuic acid.

51
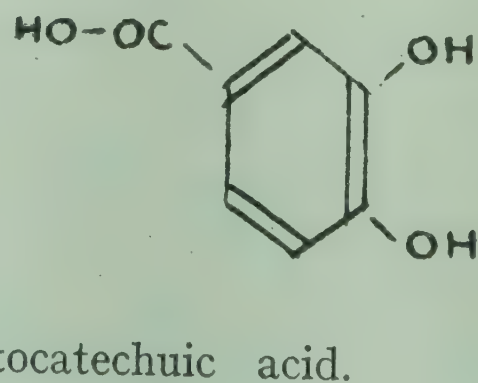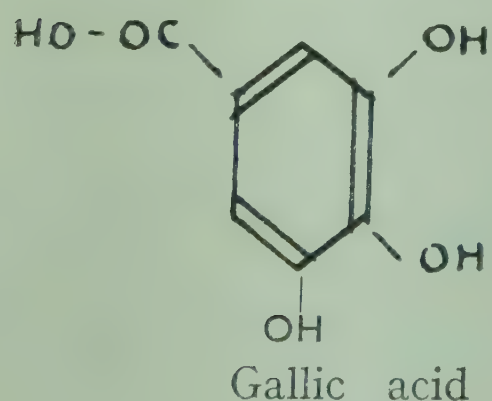
15. 2. 60

(23% / 9 780 .

This fact has been confirmed lately by A. M. Stephen[183]) of the Leather Industries Research Institute, Grahamstown, South Africa. The quantities of such pyrogallol derivatives found in Wattle Bark tannin have, however, so far been limited to a very small percentage ; by successfully improved technique they may perhaps be increased. A. M. Stephen concluded that both the catechol and the pyrogallol nuclei are present in the tannin molecule.

Some further confirmation maybe found in the considerably less intense red colouration developed in very dilute Wattle bark extract solutions as compared with solutions of Quebracho extract, when treated with nitrous acid in the presence of urea and afterwards rendered alkaline—as proposed for Spruce tannin by F. Vorsatz.[184]) Catechol itself gives a very deep colour whilst the colouration with pyrogallol is much less intense. Comparative colorimetric experiments based on these facts seemed to suggest that Wattle Bark tannin possesses approximately only half the number of active catechol units present in Quebracho tannin whilst the remainder may be pyrogallol nuclei. The observation was of interest that hydroquinone too yielded a very intense red colouration, whilst resorcinol gave no red, but a greenish-brown.

Referring back to Tea-tannin (see above under Gallotannins) it appears not to be unlikely that Wattle bark tannin contains a certain perhaps small amount of tannin such as that in tea which as related above, was by Tsujimura[185]) assumed to be a gallic acid ester of the aliphatic alcohol in normal Gambier catechin.
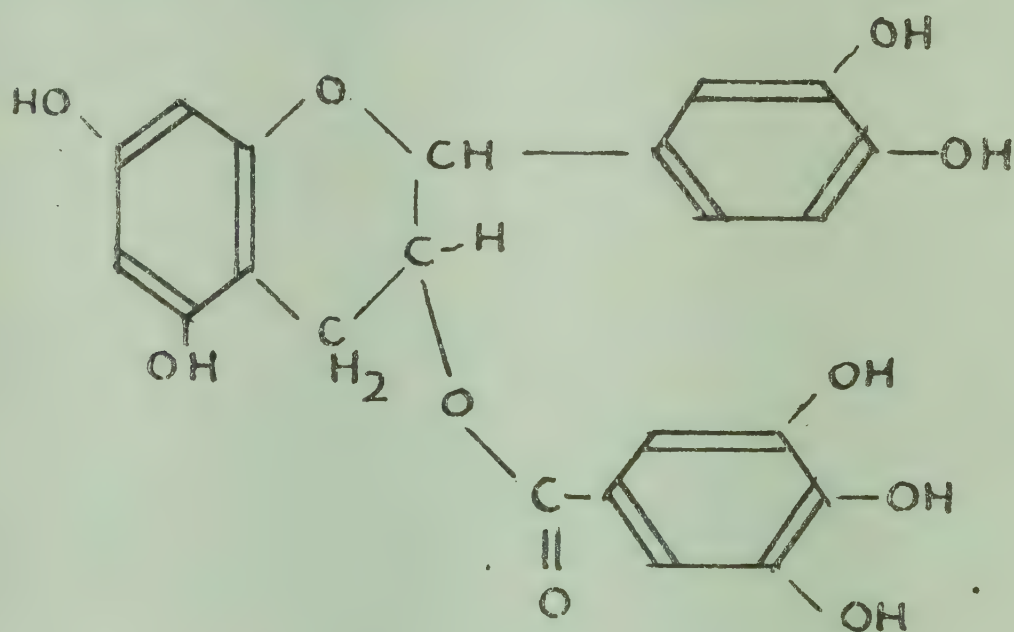
3—Galloyl—5,7,3′,4′—Tetrahydroxyflavanol.

This compound would on destructive alkaline degradation yield phloroglucinol, acetic acid, protocatechuic acid and gallic acid.

A. M. Stephen[183]) obtained veratric acid and trimethylgallic acid in approximately equal amounts, both in small quantities ; that may indicate that in a certain percentage not yet ascertained of the total tannin both acids, and thus both catechol and pyrogallol or the galloyl radical may be present.

.In order to prove the presence or absence of glucose in Black Wattle bark tannin, G. S. Tarboton[186]) attempted to hydrolyse purified tannin with hydrochloric acid of different concentrations. The reaction products were treated with Fehling's solution. The quantities of cuprous oxide obtained were either nil or infinitesimal and seemed to prove the absence of reducing sugars in the make-up of the tannin. Nor, it seems, was gallic acid split off, as in G. S. Tarboton's opinion it would otherwise have been detected by its reducing action. Enzymatic hydrolysis would probably confirm these results.

J. C. Watson[186]) found that pentoses as contained in Black Wattle bark, can under favourable conditions, particularly at temperatures above 100°C. and under pressure, generate furfural which to a certain extent combines with the tannin and condenses it to an insoluble material that may be deposited as sediment.

Isolation so far apparently not yet accomplished and examination of any accompanying dye may possibly assist in clearing up—partly at least—the structure of Wattle bark tannin.

Fluorescence tests carried out with Wattle bark tannin do not reveal anything of spectacular nature. Cotton wool soaked with untreated and with alkalised aqueous Wattle bark tannin solutions emit almost the same radiation—under ultra-violet light—as Urunday and Tizerah infusions, the untreated solution yielding a bright but less brilliant yellow than Urunday and Tizerah and the alkalised solution a somewhat dirty dull mauve colour. The fluorescence of cotton wool with aqueous infusions of the red heartwood of Wattle which may contain as much as 3.6% tannin or more, is the same as that of Quebracho, brilliant yellow with untreated, dull yellow with alkalised solution.

A. Russell[187]) and collaborators assign to Wattle bark tannin a structure similar to the following :—
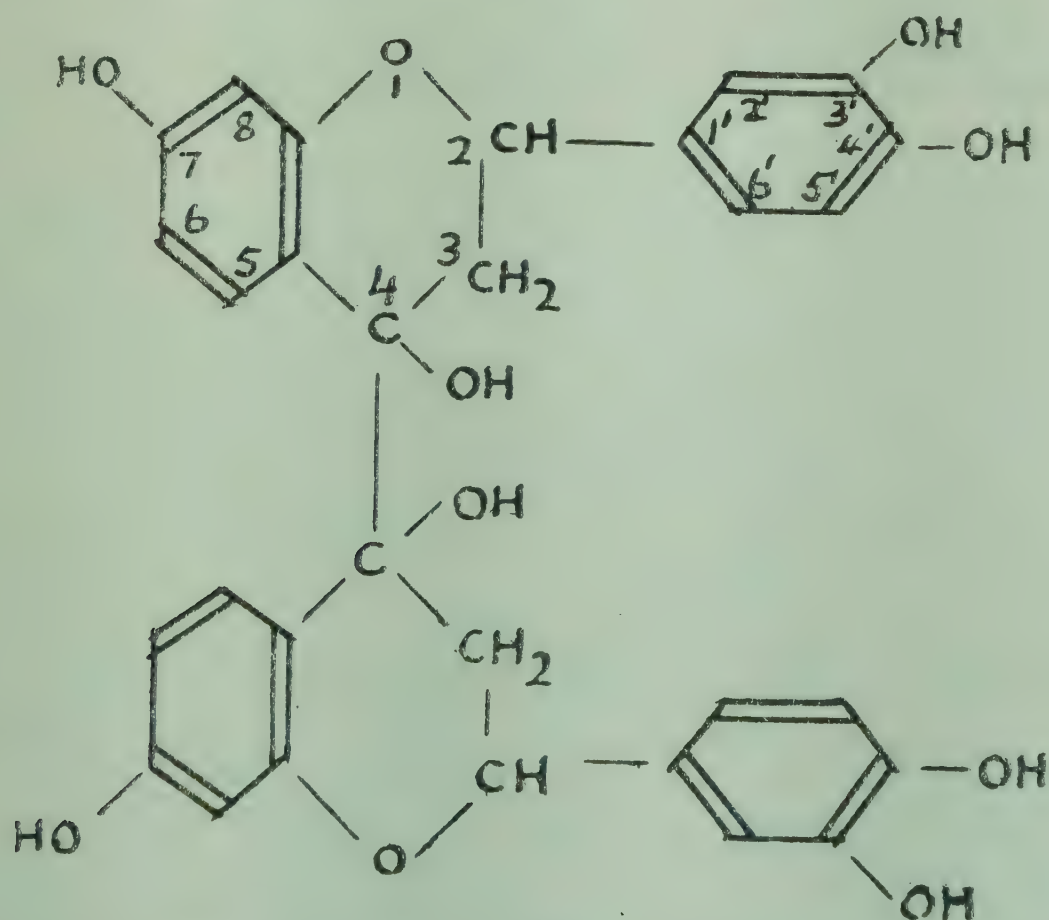
which they call bis-(7,3',4',trihydroxy) —4—flavpinacol. This compound is claimed to have been obtained synthetically by reduction with zinc dust in alcohol and acetic acid of 2,4,3',4',tetra-hydroxychalcone, and is stated to have identical properties with natural Wattle tannin, amongst which is mentioned the amorphous condition.

A. Russell[188]) also claims to have synthesised bis—(6,3',4', trihydroxy)—flavpinacol by reduction with zinc and hydrochloric acid in ethyl alcohol, of 6,3',4'—trihydroxy-flavanone or a mixture of flavanone and 3,4,2',5'—trihydroxychalcone consisting mostly of the latter and states that the light-red friable solid obtained was qualitatively indistinguishable from such natural phlobatannins as " Hemlock and Mimosa tannins." The structure of his compound would be :—
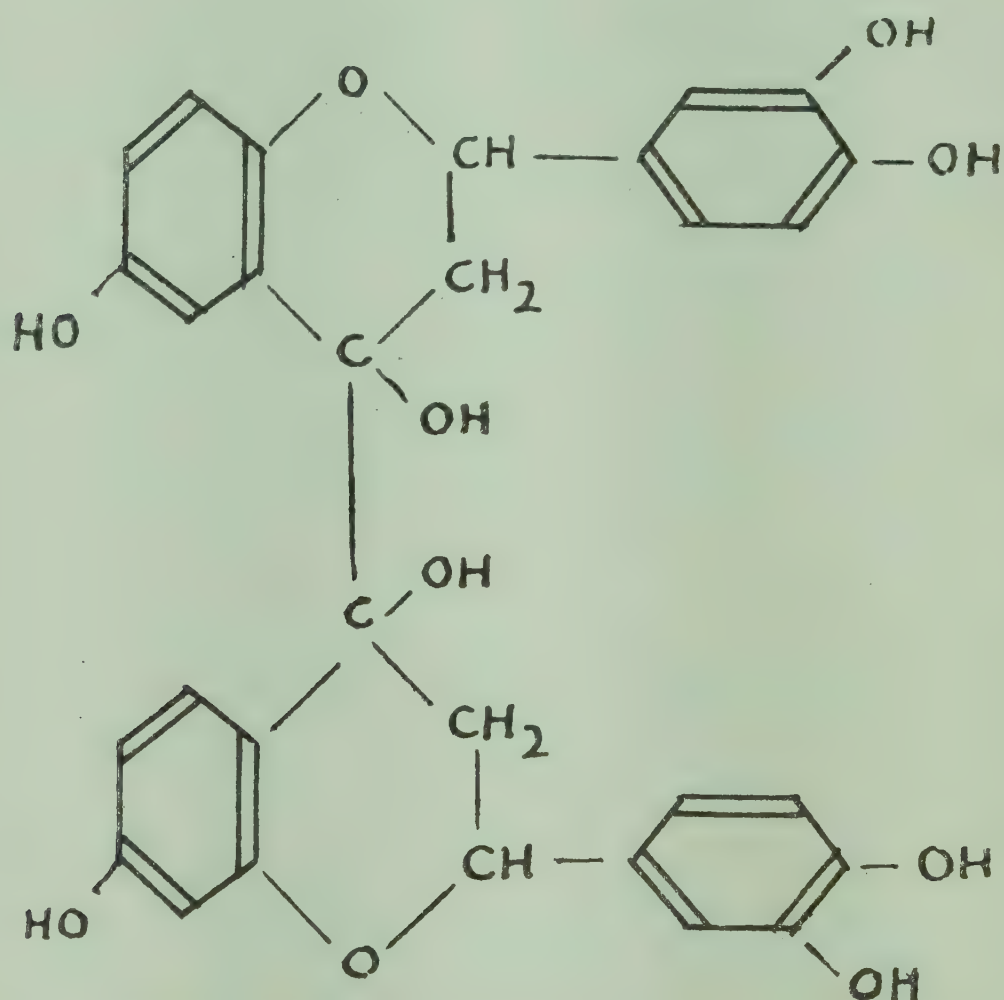
Russell's structure does not seem so far to have been universally accepted.

He claims :[193]) " the fact " . . . . " that catechin is the only member of its class known to occur naturally, whereas a large number of phlobatannins are known, makes it unlikely that phlobatannins are hydroxyflavans polymerised at the 3-position."
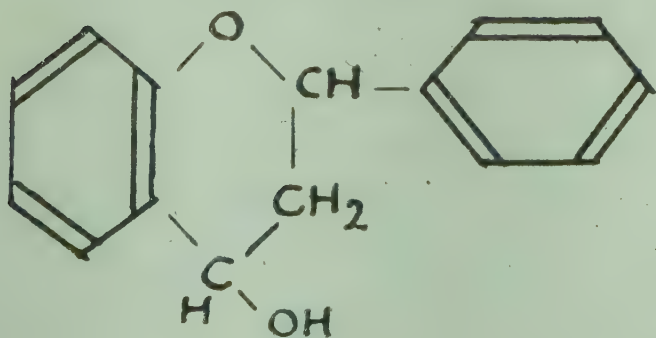
Russell's formula.   Freudenberg's formula.

54
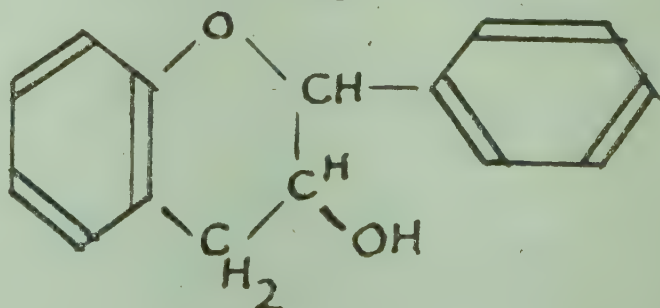
This statement by Russell does not seem to be corroborated by the facts that :

a). all the anthoxanthidine dyestuffs (found in nature and frequently accompanying the tannins) about the constitution of which there can be no doubt, as they are crystallisable, monomolecular and therefore comparatively easily definable, have the OH group in the 3-position.

b). the Quebracho tannin catechin unit has been synthesised with the OH group in the 3-position, and

c). actually another catechin with OH in the 3-position has been isolated and identified, viz. Casuarin, found in Filao (Casuarina equisetifolia),[181]) whilst in Cyanomaclurin[194]) occurring in Jack wood (Artocarpus integra) the 3-position for an OH group is assumed with probability.

It thus appears as though Russell's theory would lose at least one argument.

J. R. Nunn[189]) states that phloroglucinol had been obtained on decomposition of Wattle bark tannin with alkali ; this fact would, however, require another hydroxyl group in 5-position in addition to one in 7-position.

In a more recent publication[190]) A. M. Stephen claims to have obtained from Wattle bark tannin a comparatively high yield of resorcinol, so that so far the presence of four different polyhydroxy-benzenes has been rendered more or less probable in Wattle bark tannin, viz. catechol, pyrogallol, phloroglucinol and resorcinol.

On oxidation of Wattle tannin with concentrated nitric acid, A. M. Stephen[191]) obtained styphnic and oxalic acids, similar to the production by L. Jablonski and H. Einbeck from Quebracho, thus furnishing another proof for the presence of the resorcinol nucleus in Wattle tannin.

Molecular weight determinations carried out by A. M. Stephen [192]) showed that by raising the temperature of extraction of Wattle bark, fractions could be obtained with increasing molecular weights, rising from 1670 at an extraction temperature of 8°C. to 3230 at a temperature of 70 to 80°C.

Of additional interest regarding the constitution of Wattle bark tannin and the non-tannin in Wattle bark extract is the work carried out by T. Woodhead of the Leather Industries Research Institute, Grahamstown, South Africa.[195]) In the course of the discussion of this work T. Woodhead makes the assumption that the increase of acidity observed during bisulphitation of non-tannins and of tannins may be due to reduction of the " quinone structure " of the molecule, to hydroxy compounds. The assumption of a quinone structure

appears, however, to be new and evidence supporting this hypothesis seems to be lacking. The formula given by Woodhead is as follows :
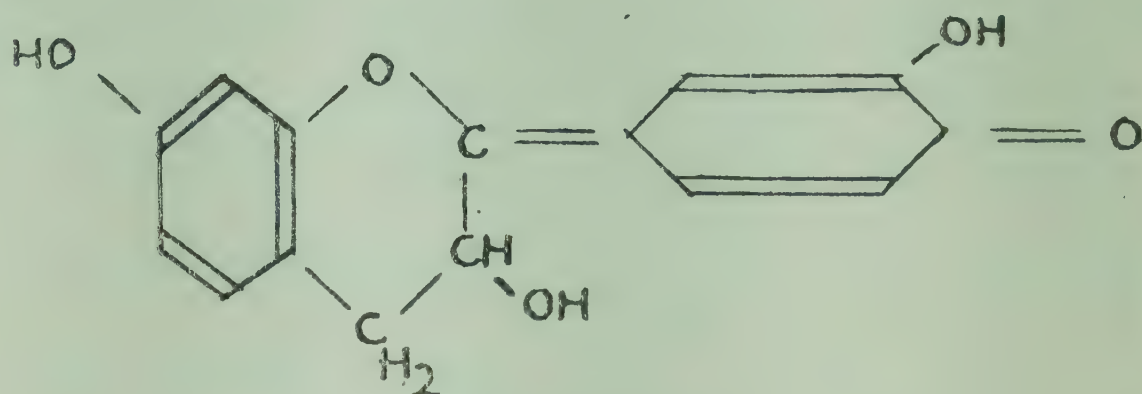
Quinone structure.

Quite apart from the improbability of the unproved quinone structure, it is more likely that any hydroxylated quinone possesses a higher acidity than the dihydroxy-benzene which Woodhead believes to be the bisulphite-reduction product (i.e. catechol).

In accordance with the stable nature of the catechol nucleus I am inclined to believe that rather than this portion of the hydroxy-flavanol compound, the already oxidised aliphatic chain in the pyrane ring is attacked if oxidation takes place at all.

It appears to me to be necessary first of all to establish without doubt the nature and the relative quantity of the fission products Wattle bark tannin may yield. It looks as if this had not been done yet satisfactorily as the available statements seem to be contradictory. The presence or absence of gallic acid radicals too, requires clearing up. As an accessory, an anthoxanthidine dyestuff, if found, isolated and identified might be helpful.

Moulding powders based on Wattle bark tannin and including resin-forming components such as phenol, aniline and cyclohexanone possess good flow and good setting powers.

The tannin in the bark of another acacia species, i.e. Acacia confusa Merr. has been studied by some Japanese writers.

Minoru Tsii and Yasuyosi Osima found in the bark 13.26% tannin and 0.12% catechin. The tannin yielded phlobaphene and d-catechin and l-epicatechin were isolated.[196]

M. Ishii believes that the tannin is probably formed by condensation of at least two to four molecules of catechin. On hydrolysis with dilute H_2SO_4 or conc. NaOH, he obtained phloroglucinol together with large amounts of phlobaphene. Oxidation of the methylated tannin yielded veratric acid. Molecular weight determination in alcohol and acetone by the osmotic pressure method, and in alcohol by the ebullioscopic method gave values of 573, 650 and 1,078 respectively.[197]

In this connection the following acacias should be mentioned : Acacia decurrens (Wendl.) Willd.—Green Wattle with up to 42%

56

tannin,[198]) A. dealbata (Page) Link.—Silver Wattle with up to 28%,[193]) A. pycnantha Benth.—Golden Wattle with up to 40.8%[198]) and even 46.8%[199]) and A. saligna Wendl.—Saligna Wattle with up to 30% tannin[198]), whilst A. Richii A. Gray from Fiji contained only 14.1% and A. horrida Willd. (A. Karroo Hayne) 18.9%.[200])

In comparison with the above, Acacia mollissima has on the average 35-38% tannin, but may go up to 48.6%.[199])

Mangrove or Borneo or Phillipine Cutch.

Barks of several members of the family Rhizophoraceae, in particular of Rhizophora Mucronata Lam., Bruguiera gymnorrhiza Lam. and Ceriops Roxburghiana Arn. Australia, Phillipines, Borneo, India, East and West Africa and Madagascar.

Very little seems to be known of the tannin in these barks.

On fusion with alkali the tannin is stated to give phloroglucinol and protocatechuic acid and on boiling with dilute sulphuric acid a phlobaphene with the composition $C_{48}H_{46}O_{21}$.[201]) It colours green with ferric salts.

To some extent, Mangrove extract resembles catechu extract (Burma Cutch) and the two tannins may perhaps—but for some accessory ingredients—be almost identical, without however being of the same degree of polymerisation.

Procter is said to have isolated from Mangrove extract a small quantity of a colourless crystalline substance resembling catechin. This find has not been confirmed.

The fluorescence of cotton wool treated with Mangrove solutions was found to be rather non-characteristic, mainly a dull yellow, both with normal and with alkalised solutions, but sometimes showing an additional mauvish tinge.

Owing to the great multitude and variety of species of plants called Mangrove which possibly not only vary in respect of their tannin content but also perhaps with regard to the class of tannin and/or the accessory ingredients, any investigation of the chemical nature of "Mangrove" tannin should be strictly confined to one species only.

Mangrove tannin is not considered to be a first-class tanning agent, quite apart from its in many cases undesirably deep colour. It would be a useful task by clearing up its chemical constitution to discover how this deficiency is caused and how it could possibly be rectified.

The properties of catalytically promoting the setting of resin-forming components in moulding powders containing Mangrove tannin are also poor, probably due to some peculiar chemical structure.

Spruce.

Bark of Picea Abies (L.) Karst. (P. excelsa Link) of the family Pinaceae.

57

Both bark and bark extract are widely used on the European continent. They are the tanning materials that in England erroneously are called " pine bark " and " pine bark extract " respectively.

The tannin content in Spruce bark as stated in the literature varies a great deal, but is seldom stated to be more than 13%. Aqueous extracts show varying amounts of insolubles.

W. Grassmann and W. Kuntara[202]) have found that in addition to the tannin as indicated by the Official Method of Tannin Analysis and in general more or less extracted by diffusion with water, a considerable quantity of tannin is present in the bark which under usual conditions is not extracted with water and is not utilised, but which can be rendered available by subjecting the bark to heating, steaming or to a treatment with enzyme poisons as soon as possible after felling the tree or after removing the bark from the wood. According to the authors mentioned, the tannin which is originally water-soluble, after cutting off the natural sap flow, is—chiefly due to the action of enzymes present in the bark—rapidly converted into phlobaphenes which are insoluble in water.

By the above methods of preservation, the authors were able to increase the tannin yield in some cases by even more than 100%.

It appears likely that such methods should particularly be applicable to barks, leaves and other parts of plants which contain flowing sap and less to woods and especially heartwoods, as in the latter we can probably assume that the deposition of tannins has arrived at a more or less definite endpoint and that the tannin does not any longer undergo a further transformation. It would, however, be worth while investigating the effects of the above methods on the tannin in heartwoods as well, as soon as possible after felling and in various layers of different ages.

There is very little known about the chemical nature and the structure of spruce tannin. It is certainly a flavotannin yielding phlobaphenes, condensing with aldehydes and acids to insoluble bodies.

Spruce tannin is in so far remarkable as the filtrate from the formaldehyde-acid precipitate sometimes gives a blue colouration with ferric salts and it may therefore be suspected to contain a pyrogallol nucleus besides the catechol nucleus. A. Russell[203]) states that the fission products are protocatechuic acid and phloroglucinol, but whether a phloroglucinol nucleus is present does not seem to have been definitely established. The so-called phloroglucinol test (use of a splinter or shaving of spruce wood and subsequent treatment with hydrochloric acid) is unreliable as also other phenols, respectively phenol derivatives show this reaction, besides phloroglucinol. And in the case of the alkaline fission-products of spruce bark tannin the reaction appears to have been rather moderate only, whilst e.g. Quebracho yielded a very strong reaction,[204]) although Quebracho tannin does not contain phloroglucinol.

Böttinger[205]) gives spruce bark tannin the problematic formula

$C_{21}H_{20}O_{10}$ and to the acetyl derivative of spruce " reds " he attributes the formula $C_{42}H_{27}(C_2H_3O)_7O_{17}$.

According to M. Nierenstein[206]) ellagic acid is also present in Spruce bark.

Fritz Vorsatz[184]) bases a colorimetric method of estimating the tannin in Spruce bark extract on the assumption that this tannin contains a catechol nucleus. He compares the solutions to be tested for Spruce Bark tannin, with standard solutions of pure catechol and thereby finds a content of 30% to 35% catechol which is a little less than what would be expected from Freudenberg's Quebracho catechin formula.

The fluorescence of cotton wool treated with aqueous spruce bark infusion is a brilliant blue and that obtained with an alkaline infusion a bright bluish-white ; it is thus quite different from those obtained with Quebracho, Tizerah, Urunday and Mimosa.

Hemlock.

Bark of the hemlock fir Tsuga canadensis (L.) Carr. (in the Eastern part of the United States) and Tsuga heterophylla (Raf.) Sarg. (in the Western part of the U.S.A.) of the family Pinaceae with up to 14% tannin.

Hemlock extract usually contains a considerable amount of insolubles or " phlobaphenes," which is increased by heating with acid. Formaldehyde renders the tannin insoluble.

Böttinger[207]) attributed the formula $C_{40}H_{30}O_{17}$ to Hemlock phlobaphenes and $C_{20}H_{18}O_{10}$ to the tannin itself.

A. Russell[208]) believed to have synthesised an amorphous tannin identical with Hemlock tannin and assigned to it either of the two following flavpinacol structures :

or

HO OH O CH — OH — OH

CH₂

C OH

C OH

CH₂

CH — — OH

HO O OH

OH
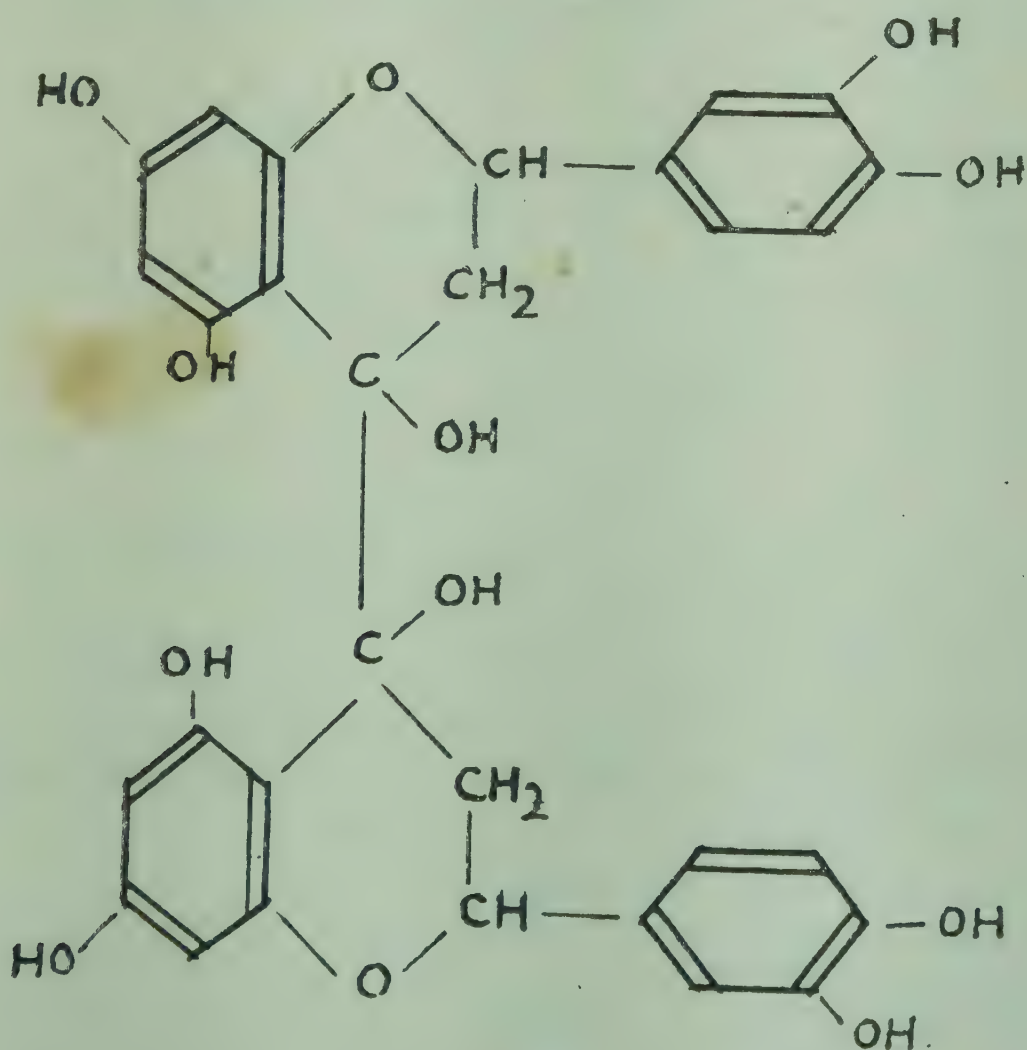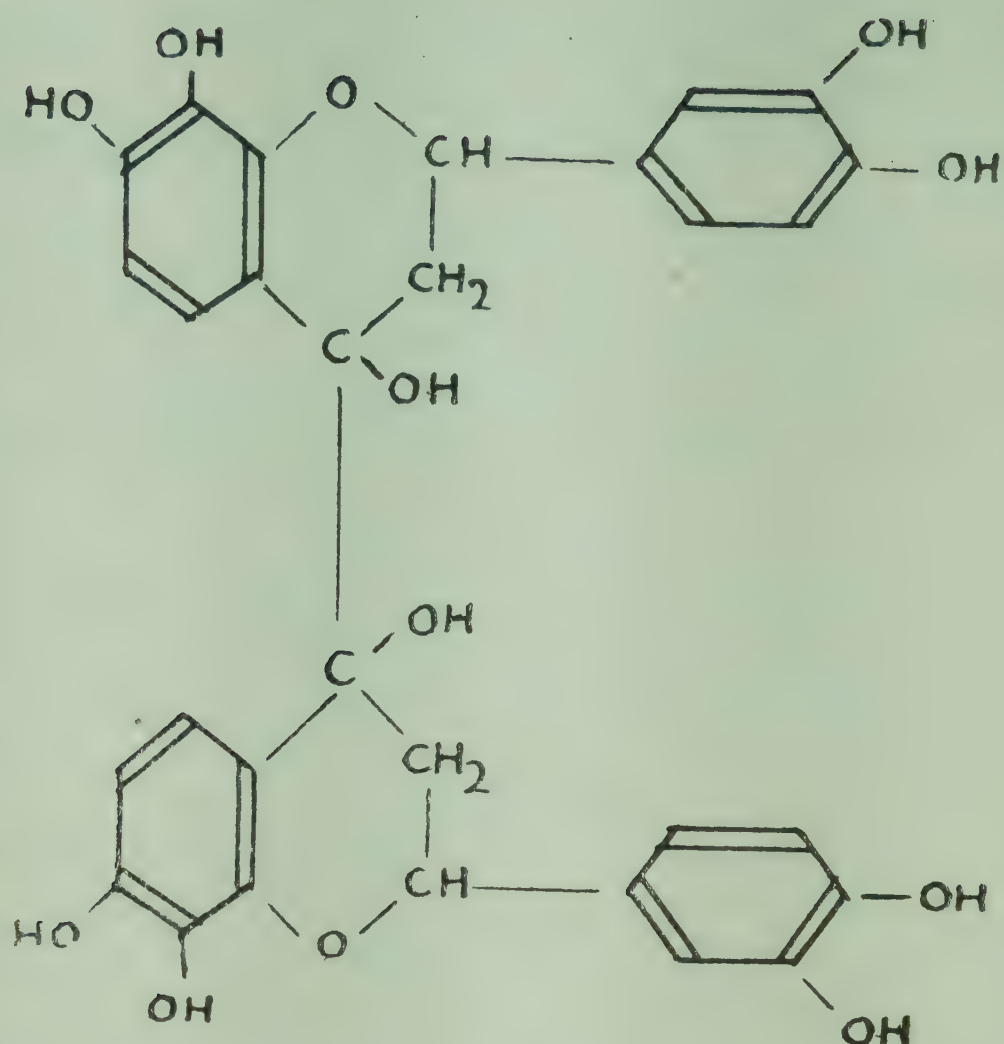
The fission products with fused alkali of Hemlock tannin seem to be protocatechuic acid and pyrogallol. Repeated examination yielded no phloroglucinol. These facts should point to the second formula.

But Russell's flavpinacol-structure formula does not seem to be fully proved yet. It is therefore perhaps as well possible that the tannin in hemlock is based on a new form of catechin with the following structure :

HO OH O CH — OH — OH

CH

C OH

H₂
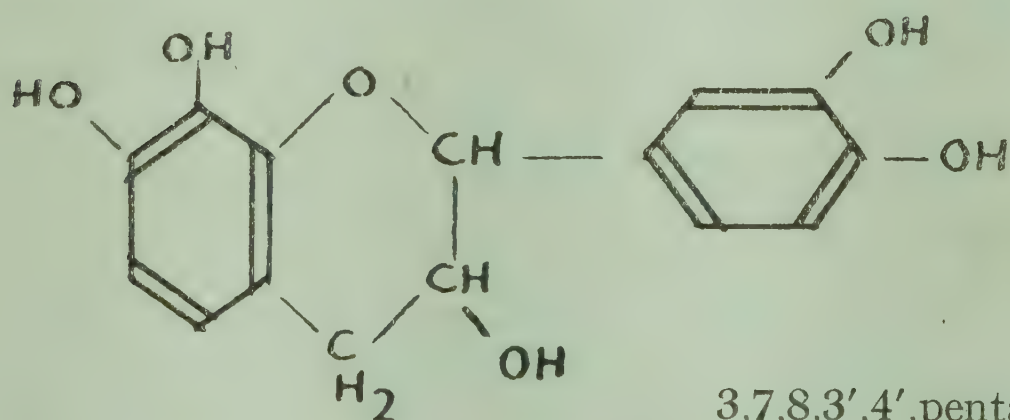
3,7,8,3′,4′,pentahydroxyflavane

The absorptive fibre fluorescence of Hemlock extract is in the literature described as insignificant and uncharacteristic. Cotton wool impregnated with an aqueous Hemlock bark infusion irradiated by ultra-violet light emits a brownish light, irregularly mixed with indistinct yellow patches.

Larch.

Bark of Larix decidua Mill. (L. europaea DC.) and Larix sibirica Ledeb. of the family Pinaceae. Particularly these two species have great importance for Russia, covering more than 400 millions of acres in Russia and Siberia.[209]

Besides the facts that the tannin forms " reds " and that it colours ferric salts green, hardly anything seems to be known about it. The fission products seem to be protocatechuic acid, respectively catechol and phloroglucinol.

The fluorescence of cotton wool soaked with larch bark infusions and washed, is bright blue, whilst alkalised infusions give a pale blue fluorescence.

Spruce and Larch tannins seem therefore to form a special class, as their fluorescence is obviously of quite a different character from that of Quebracho, Tizerah, Urunday and Mimosa.

Willow.

Bark of several Salix species of the family Salicaceae, in particular Salix viminalis L., repens L., fragilis L. and caprea L.

According to K. Nechaev and coll.[210] the barks of different willows contain an average of 10.5% tannin.

The tannin is precipitated from boiling aqueous solutions with sulphuric acid and with formaldehyde and hydrochloric acid. It yields a green colour with ferric chloride. A. G. Perkin[211] says the tannin is a glucoside. Powarnin and Shurawlew[212] obtained in decomposing tannin of Salix alba L. x viminalis L. protocatechuic acid, pyrogallol, phlobaphenes and sugar.

Votocek and Köhler,[213] on fusion of purified tannin from Salix purpurea L., obtained in one instance a material which gave the reactions of catechol, and in another instance a material that showed the reactions of both phloroglucinol and protocatechuic acid.

According to a general statement by A. Russell,[214] protocatechuic acid and phloroglucinol are obtained from Willow.

Obviously more work is required to clear up not only the constitution and structure of the Willow tannin, but also the simple products of decomposition.

Cotton wool impregnated with aqueous Willow Bark infusions exhibits a distinct yellow, but not very bright fluorescence, whilst after treatment with alkali the fluorescence is rather indistinct.

Avaram.

Bark of Cassia auriculata L. of the family Leguminosae. South and West India and Upper Burma. (Also called Avla, Turwad and Turwar).

Contains about 17%[215] and sometimes up to 29%[216] tannin and has been used particularly in the Madras district for the manufacture of East India Kips. Avàram has formerly been one of the

most important materials of India; it is still extensively used in India, but supplies have to some extent been depleted.[217]) It is now largely displaced by Wattle bark.[218])

The tannin is stated to be a "catechol tannin," but nothing else seems to be known about its nature.

Flavotannins of Minor Commercial Importance.

There are a great many species belonging to this group of which only a limited number can be mentioned. Besides the fact that these tannins are of the "catechol" or flavotannin class, very little has been published about them. In a few instances, however, a closer investigation has been made and has resulted in an interesting addition to previous knowledge.

The following plants are members of this group:

Alder
Algarrobo Negro
Birch
Canaigre
Wild Cherry
Cu-Nao
Elandsbean
European Dock
False Acacia
Fern
Gedari
Guayacan
Horse Chestnut
Hottentot Fig
Ironwood of Malabar
Jack-tree
Mangue
Redwood
Rhatany
Sanya
Teak

Alder.

Alnus glutinosa (L.) Gaertn. and incana (L.) Moench of the family Betulaceae, in bark and fruits up to 16% or even 20% tannin.[219]) Fission products: protocatechuic acid, Phloroglucinol, Acetic acid, Catechol. Mineral acids liberate sugar. Colours green with ferric salt.

Algarrobo Negro.

Wood of Prosopis nigra Hieron., belonging to the family Leguminosae. South America.

Solid extracts have been manufactured with up to 45% tannin[220]) but seem to be used mainly as mordanting and dyeing agents.[221])

Birch.

Betula alba L. (= B. pendula Roth and B. pubescens Ehrh.) and lenta L. of the family Betulaceae. Bark contains up to 16% tannin.[222]) Fission product : Catechol.[223])

Canaigre.

Red dock, Rumex hymenosepalus Torr. of the family Polygonaceae. The Mexican popular name is Raiz colorada. The rhizomes are stated to contain up to 30% tannin and even more, [224])[225]) depending on the age of the plant.[226]) Mexico, California and Texas and other parts of the South Western United States. Wild roots seem to contain a higher percentage of tannin than cultivated roots.[227])

Fission products : Protocatechuic acid, catechol, no phloroglucinol. Heating the tannin with acids produces reds but no sugar. Ferric salt : green colouration. Some carbohydrates and particularly starch and sugars[226]) seem to accompany the tannin which fact may be the reason why the tannin is readily soluble in water and penetrates hide quickly, probably due to peptisation.

Wild Cherry.

Prunus avium L. of the family Rosaceae. Bark contains only a small amount of tannin, but which sometimes rises to 16%.

With acids : " Reds " ; no sugar. Ferric salt : green.[228])

Cu-Nao.

Also called False Gambier. Dried tubers of Dioscorea atropurpurea Roxb. of the family Dioscoreaceae. French Indochina.

Tannin content was found to be 38% at 19% moisture.[229]) This material seems to have been used in China for many generations for the dyeing of silk and cotton and for the preservation of sails and fishing nets.

Because of the relatively high content of starches, leaching is best carried out at first at room temperature and later on at about 50°C.

The tannin may contain a slight admixture of gallic acid or of gallotannin.

Elandsbean.

Tuberous roots of Elephantorrhiza Burchellii of the family Leguminosae. A small shrub growing in South Africa. Tannin content found between 15.6%[230]) and 21.7%[231]). The roots contain a comparatively high amount of matter that at normal temperature is insoluble, but soluble at elevated temperature (probably phlobaphenes). The non-tannins seem to comprise a high percentage of sugars.

Stems, leaves and seed pods too seem to contain appreciable amounts of tannin (13% and 5% respectively).[230]

European Dock.

Several species of Dock of the family Polygonaceae with up to 22%[232] tannin in roots. Tannin stated to be very similar to Canaigre, but on the other hand, to be related to tannin in Polygonum bistorta which is a gallotannin containing ellagic acid.[233]

One species, the so-called Great- or Giant Water Dock, Rumex hydrolapathum Huds. grows in Germany and Hungary and has been cultivated with the result that " water plants " yielded 12.4 to 21.6% tannin and " dry-land plants " only 6 to 8%.[234]

False Acacia.

Robinia pseudoacacia L., a member of the family Leguminosae, in England called false acacia, in the United States black locust. It contains in different parts of the plant various flavane derivatives.

The flowers[235] contain robinin = a glucoside of Kaempferol (also called robigenin) :[236]

= Kaempferol
(Trihydroxyflavonol)
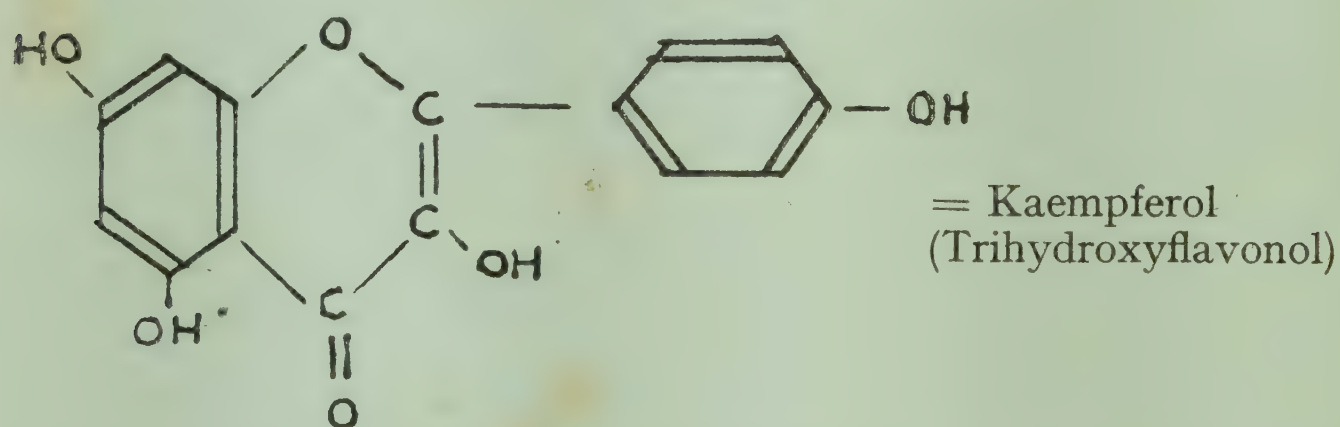
This is the only glucoside besides xanthorhamnin that on hydrolysis yields three sugar nuclei, viz., 2 molecules of rhamnose and 1 molecule of glucose.[237]

The leaves[238] contain acacetin which is a monomethylether of the dyestuff apigenin :

Acacetin

64
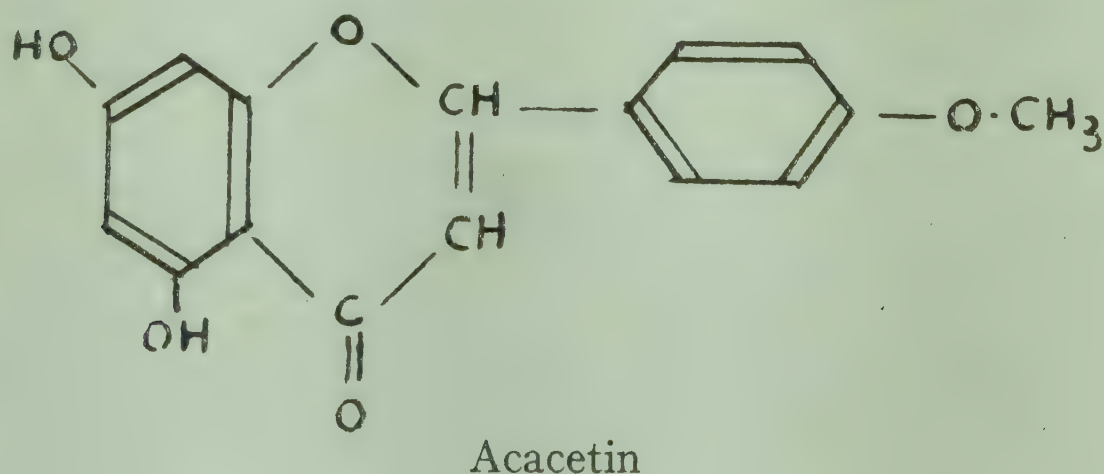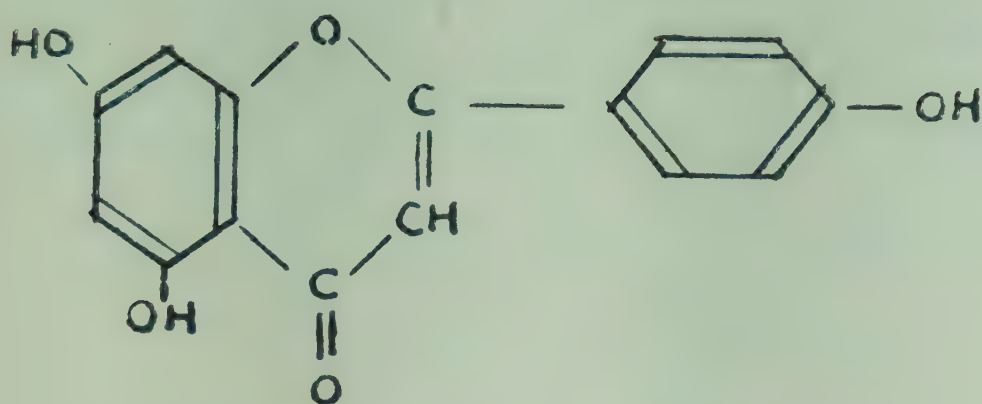
Apigenin = Trihydroxyflavone.

The bark[239]) appears to contain acacetin[240]) and a small quantity of a flavotannin which possibly has as mother substance the corresponding catechin :
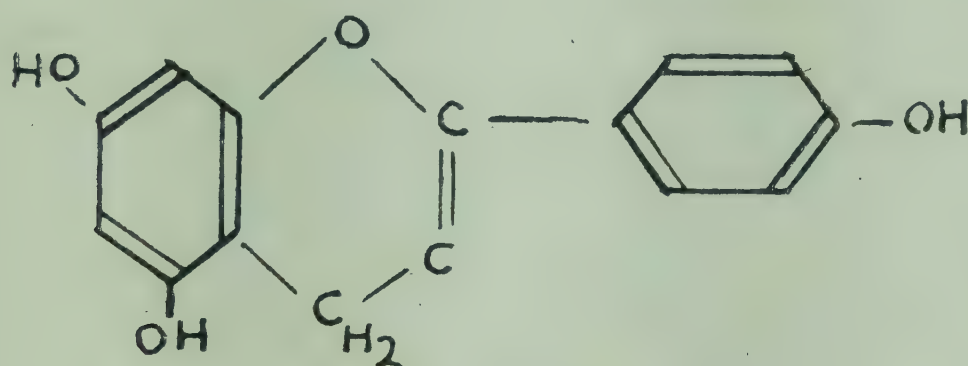
Trihydroxyflavene

or
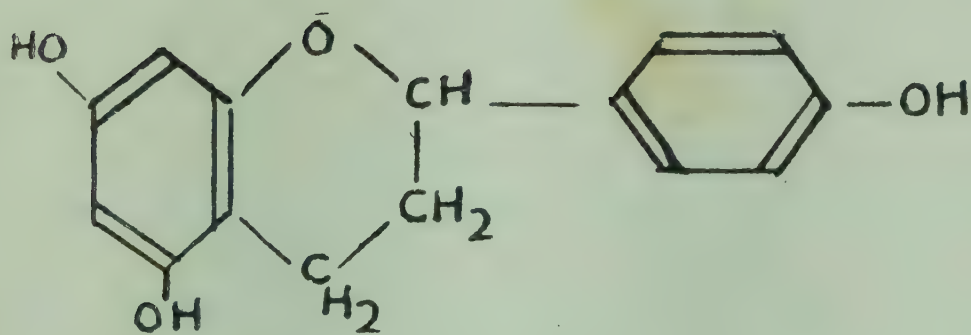
Trihydroxyflavane

The heart wood[241]) too has a small quantity of a tannin which is said to have the character both of a " catechol " and a " pyrogallol " tannin. In addition, the wood[242]) is stated to contain the two above mentioned dyestuffs, viz., robinin and acacetin, and a third dyestuff called robinetin[243]) of the following constitution :

65
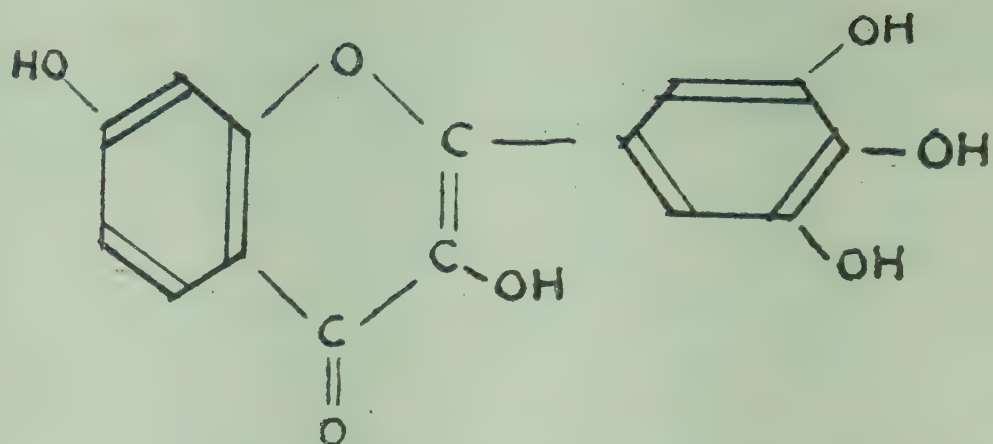
=Robinetin (Tetrahydroxyflavonol)

which possesses a pyrogallol and a resorcinol nucleus. The tannin in the wood is perhaps based on this type of structure and the corresponding catechin has possibly the following constitution :
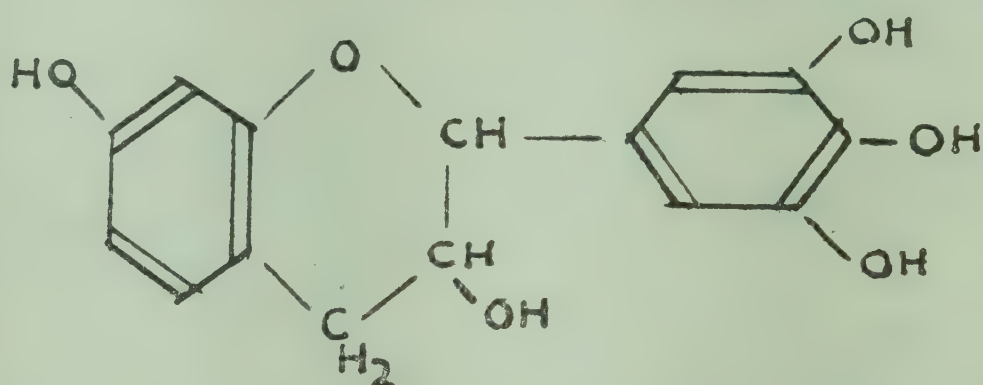
= Tetrahydroxyflavanol.

Robinia pseudoacacia would thus be a tree bearing two different types of tannin so far not encountered in other plants and three different yellow dyestuffs of the anthoxanthidine type. Though hardly of any commercial importance, it seems to be of extreme scientific interest.

Fern.

Rhizomes of Dryopteris Filix-mas (L.) Schott and others of the family Polypodiaceae.[244] Tannin content up to 10%.

Fission products : Protocatechuic acid, phloroglucinol.

With acids : " Reds." Ferric salts : Green.

Sugar has been found by some authors, but this has not been confirmed. The tannin is stated to contain a certain amount of nitrogen.

Gedari.

Root, bark and wood of Rhus oxyacantha Cav. of the family Anacardiaceae.[245] Libya and Syria.

The bark contains approximately 17% tannin, the wood up to 12%. The tannin is stated to be similar to Quebracho, but the ratio of tannins to non-tannins is comparatively low, about 2.6 to 2.8 only, whilst the colour is high.

66

On fusion with potash, it is stated to yield protocatechuic acid and resorcinol. Phloroglucinol too seems to have been found in the products of decomposition.

Extracts are said to have been made which showed a high ratio of non-tannins.

The bark infusion is stated not to yield any fluorescence, whilst the wood extract gives a strong yellow fluorescence.

The extracts contain a high percentage of insoluble matter which, as it is the case with Quebracho. lends itself to solubilisation by means of bisulphite.

The bark of another Rhus species, viz., Rhus Thunbergii Hook, now classified as Heeria argentea (E. Mey.) Meisen, is noted for its high tannin content. This is a short stumpy tree growing in South Africa. C. O. Williams gives 35% tannin as an average of several samples.[246]

Guayacan.

Wood of Caesalpinia melanocarpa Gr. of the family Leguminosae, Argentine. Tannin content in the wood about 13%.

With acids: " Reds." With Ferric salts: Green.

Acid and formaldehyde precipitate the tannin completely.

The fluorescence of cotton wool soaked in aqueous solutions of Guayacan is a brilliant violet. It would be interesting to search for dyestuffs contained and their nature.

The tannin in Guayacan wood shows the " catechin effect," i.e. it is capable of promoting the themosetting of resin-forming components and may therefore contain a resorcinol or a phloroglucinol nucleus.

Horse Chestnut.

Bark and other parts of Aesculus Hippocastanum L. of the family Hippocastanaceae.

Fission products are protocatechuic acid and phloroglucinol. With acids: Reds. With Ferric salts: Green.[247]

Flowers contain quercetin.

Hottentot Fig.

Mesembryanthemum eduli L. of the family Aizoaceae. California. The dry leaves are stated to contain 19.4% tannin and the dry stems 14.2% both of the " catechol " type, suitable for the production of leather. The yield of cultivated land is said to be 1,500 lbs. per acre.[248]

M. Nierenstein asserts that the leaves and the bark of the Hottentot Fig tree contain a tannin which on hydrolysis with tannase yield gallic acid and a catechin-like substance.[249]

Ironwood of Malabar.

The bark of Hopea parviflora Bedd. of the family Dipterocarpaceae, India, has a tannin content of up to 25.8% together with a favourably low percentage of non-tannins. (6%).

67

Formaldehyde-acid :—Precipitate ; the filtrate yields no colouration with iron.

Ferric salts : Greenish black colour.

Solid extracts seem to have been made with 65.9% soluble tannin, 21.6% nontannins, 2.6% insolubles at a moisture content of 9.9%.[250])

Jack-Tree.

Artocarpus integra (Thunb.) Merr. of the family Moraceae (India, Malaya) contains in wood,[251]) leaves and root bark some tannin, the dyestuff Morin and Cyanomaclurin. The latter is a catechin-like substance which on fusion with caustic, yields phloroglucinol and β-resorcylic acid instead of protocatechuic acid (as with catechin) and on distillation yields resorcinol.[252]) Its formula is $C_{15}H_{12}O_6$ and it has probably the following structure :—
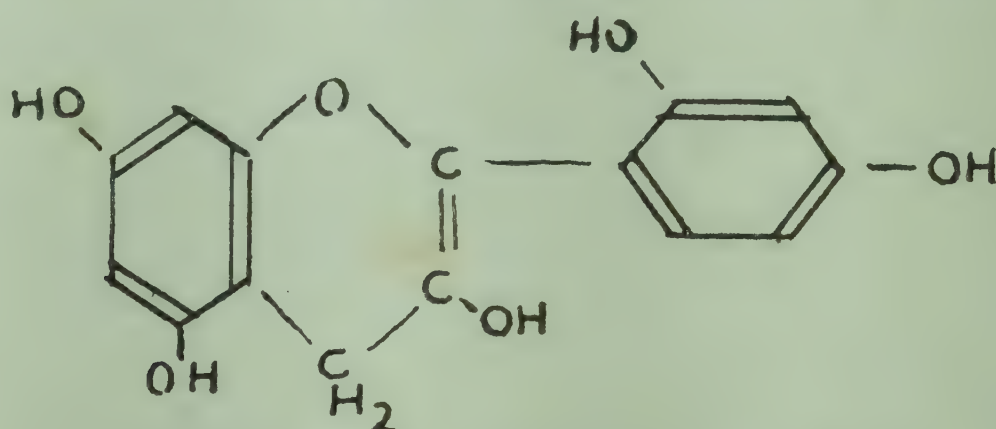
= Cyanomaclurin (Tetrahydroxyflavenol)

Cyanomaclurin must have 2 hydrogen atoms less than catechin and therefore a second double bond in the pyrane ring in addition to that already existing in catechin. It gives the phloroglucinol test with spruce shavings and hydrochloric acid. Ferric chloride colours violet just as resorcinol does.[253]) Mineral acids produce difficultly soluble or insoluble redbrown " Reds."[254])

The above mentioned yellow dyestuff Morin has the corresponding anthoxanthidine structure and yields the same fission products as Cyanomaclurin.
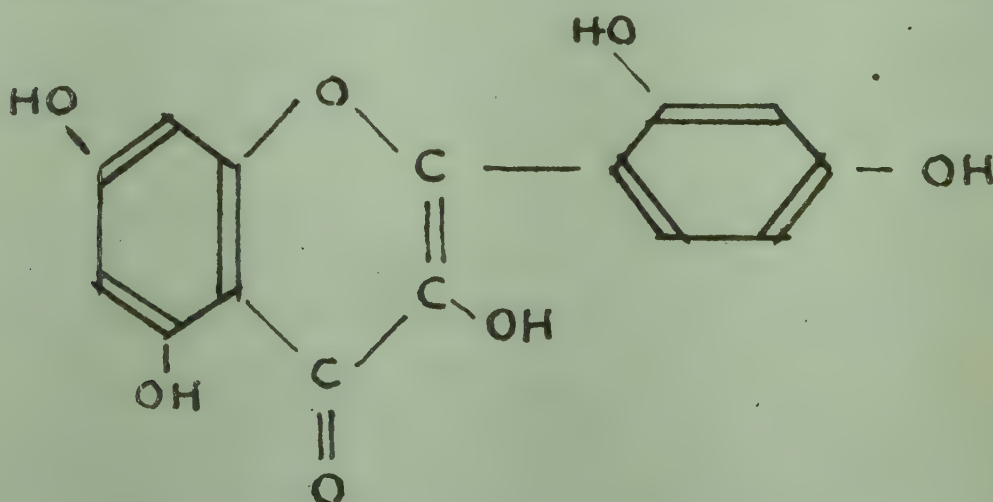
Morin (Tetrahydroxyflavonol)

68

Mangue.

Bark of Laguncularia racemosa Gaertn. f. of the family Combretaceae, occurring in Brazil, the West Indies and West Africa. Two Brazillian varieties are mentioned, i.e. Mangue Sabateiro with about 18% tannin and Mangue Vermelho with 29% tannin.[255]

In Jamaica, it is called " White Mangrove," on account of the light colour it imparts to leather.

M. Nierenstein[256] found in " white mangrove " bark from the West African coast, a " catechol tannin " stated to have formed a bloom-like deposit, which was a yellow colouring matter belonging to the flavones. It was probably an anthoxanthidine dyestuff. Nothing else is known about the structure of the dyestuff.

The bark is stated to contain a high percentage of mineral matter[255] which is a feature in common with mangroves.

Besides the fact that the tannin belongs to the " Catechol " class nothing seems to be known about the chemical structure of it.

The wood and leaves of this plant contain gallotannin.

M. Nierenstein identified laguncurin occurring in White Mangrove bark as maclurin $C_{13}H_{10}O_6$[257] identical with " Kino Yellow " as occurring in the kino of Eucalyptus hemiphloia F. Muell.

Californian Redwood.

Bark and wood of Sequoia sempervirens (Lamb) Endl. of the family Taxodiaceae. Western United States.

Bark and wood seem to contain varying amounts of tannin. One sample of bark from a large branch was found to contain 4.3%, whilst both the true heartwood and the pseudoheartwood had only 1.9%. Scalione and Merrill[258] had, however, found 12.2% in heartwood.

As far as the low tannin content is concerned, the tree does not seem to possess commercial importance ; it has been included in this survey because it occurs in considerable numbers in the Western United States where, growing to extreme heights and diameters it is of great importance as a valuable timber and also because the tannin shows some peculiar interesting features which somehow appear to point to a " Mixed " tannin.

The tannin in the bark is completely precipitated with formaldehyde and acid and the filtrate from this precipitate is colourless and does not give any colour reaction with iron alum. The untreated aqueous infusion, however, gives a somewhat bluish (blackish) colouration.

The aqueous infusion from the heartwood gives a green colour with iron alum, but is not completely precipitated with formaldehyde and acid, whilst the filtrate is strongly coloured (orange) and with iron yields a green colouration.

On boiling with dilute acids, aqueous infusions of both wood and bark produce some " Reds," that from the heartwood being very dark, almost black.

Scalione and Merrill[258]) obtained from heartwood a tannin that showed the reactions of a " Pyrogallol " tannin.

From the cones of another species of the same genus, viz. of Sequoia Wellingtonia Seem. (Sequoia gigantea (Lindl.) Decne.), a so-called "Sequiatannic acid" was isolated by Heyl which according to A. G. Parkin and A. E. Everest[259]) on boiling with dilute sulphuric acid, yielded a phlobaphene, gallic acid and sugar.

The fluorescence colour of cotton wool impregnated with aqueous infusions from Sequoia sempervirens, both of bark and of heartwood (both normal and after treatment with alkali) is uncharacteristic and indistinct.

Moulding powders have in America been made with the wood of Redwood.[260]) They appear not to be based on such properties of flavotannins as described for instance in the chapter on Quebracho, but on a peculiar thermoplastic property alleged to be inherent in Redwood.

M. A. Buchanan, H. F. Lewis and E. F. Kurth[261]) describe the preparation of " true " tannin and of phlobaphene from old stump wood of Sequoia sempervirens. They found 2.0% purified tannin and 4.3% purified phlobaphene, both as ether-insoluble fractions.

According to these authors, Redwood tannin belongs to the " phlobaphene " class, and contains a small, but appreciable amount of methoxyl, whilst their phlobaphene contained 30-35% of native lignin. The alleged thermosplaticity of Redwood may perhaps partly be caused by this methoxyl and lignin content.

Both tannin and phlobaphene yielded protocatechuic acid and catechol on fusion with alkali, whilst by destructive distillation, catechol and small quantities of phenol were obtained.

The authors state that the phlobaphene appears to be a condensation product of the tannin in which both phenolic and aliphatic hydroxyl groups are involved.

In general, it may perhaps be said that the tannin in Redwood seems to have undergone a remarkable degree of transformation in the direction of insolubilisation both by condensation and polymerisation and by methylation of hydroxyl groups with the effect that a material has been produced that is similar to lignin, although not quite so insoluble.

Rhatany.

Root and particularly root bark of Krameria triandra Ruiz and Pav., a shrub of the family Polygalaceae, growing in Peru and Bolivia. Up to 40% of a light yellow tannin are stated to have been found which in aqueous solution gives a green colouration with ferric chloride.

70

It yields a phlobaphene called " Rhatany Red." On dry distillation catechol is produced, whilst alkaline fusion yields protocatechuic acid and phloroglucinol. The presence of sugar which previously was stated to have been obtained has been rendered doubtful.[262])

D-Gambier-catechin and dl-Gambier-catechin are stated to be present in the root.[263])

Sanya.

Native name Mopane, also called Turpentine tree.

Wood and bark of Copaifera Mopane J. Kirk of the family Leguminosae. Central Africa. (Congo, Nyasaland). Wood with 10.9% and bark with 16.6% tannin.

With iron salts : Green, with acids : " Reds."

The absorptive fibre fluorescence with the aqueous infusion from the bark is white, whilst that from the wood is whitish yellow. The alkalised wood infusion gives a dull yellow flourescence.

Copaifera Mopane is one of the sources for Congo copal.[264])

The bark from another species, viz. Copaifera Langsdorfii Desf. is also stated to contain 16.6% tannin.[265])

Teak.

Bark of Baikiaea plurijuga Harms., so-called Rhodesian Teak, of the family Leguminosae. Rhodesia. This bark was found to contain 26.0% tannin at a moisture content of 10.5%. The tannin belonged principally to the flavotannins. J. R. Furlong in " Tanning materials of the British Empire "[266]) mentioned a tannin content of 10% in wood and of 20% in bark, C. O. Williams in " South African Tanning Materials "[267]) 19.9% in bark and 11.3% in wood.

The bark tannin is strongly coloured which fact renders the exploitation of the bark almost impracticable. Attempts by the writer to decolourise the extract failed, but a considerable degree of decolourisation was achieved when it was carried out during extraction.

Teak wood as used in the timber trade, in particular of Moulmein quality (Tectona grandis L.f. of the family Verbenaceae) was found to contain very insignificant amounts of tannin ; one sample had only 0.64% of a tannin which with iron alum gave a green colourisation and showed a bluish fluorescence on cotton wool.

Another variety, known as Iroko Teak had a little more tannin (of the flavotannin class) and yielded a violet fluorescence. This sample seemed to have been from Chlorophora excelsa (Welw.) Benth. and Hook. of the family Moraceae. Bark from this tree was supplied under the name Mvule and had only 0.9% tannin.

" MIXED TANNINS "

GENERAL.

Mixed tannin is a term which hitherto has, in general, been applied to tannins about the constitution of which usually not much was known and in respect of which nobody actually knew whether they belonged to the gallotannins or to the flavotannins. The term originated from the fact that although these tannins produced " Reds " or phlobaphenes they also gave a deep blue colouration with ferric salts and thus at the same time appeared to belong to the " pyrogallol " class.

Recently, however, some important knowledge has been gained in respect of a few of these so-called " mixed " tannins.

When remarking on oak bark tannin which used to be called a mixed tannin, I stated that Freudenberg classes it mainly as a hydrolysable tannin (or in accordance with the terminology adopted in this present essay, a gallotannin) whilst its capacity of forming insoluble products were attributed by him to higher condensation products the nature of which is as yet unknown. It is for the former reason that I dealt with oak bark tannin in connection with the gallotannins, although flavane derivatives appear to be present, perhaps even forming components of the tannin.

Another tannin has already been mentioned among the gallotannins that with justification could be included in the group of mixed tannins. This is the tannin in tea which has been found to be probably a gallic acid ester of flavane derivatives.

The peculiar character of a " Mixed " tannin may be due to several different possible conditions such as :

The tannin may be a real mixture of gallotannins and flavotannins. This appears to be the case with oak bark tannin.

The tannin may constitute an ester of gallic acid (or of an acid derived from gallic acid) with a flavane derivative. This seems to apply to tea-tannin.

A further possibility is the mixture of true gallotannins with esters of flavane derivatives.

In addition to these modifications, there exists the possibility that the whole or a part of the flavotannins present contains a pyrogallol ring attached to the benzodihydropyrane complex. This is likely to be the case with the tannins of Cyprus Sumac, Filao and Maletto, probably to a small extent with Mimosa tannin and perhaps with spruce tannin as well.

In deciding whether a gallotannin is present or a flavotannin, it is essential to recognise the source of any gallic acid or pyrogallol produced during treatment.

73

In building up a so-called "Mixed" tannin of the last mentioned type various units with pyrogallol rings may have been polymerised or condensed simultaneously and into the same large complex with flavotannin units containing rings other than pyrogallol.

It must be realised that any comparatively stable blue colouration produced by treatment with ferric salts is not due to pyrogallol but to gallic acid or its acidic derivatives. Pyrogallol and ferric salts (iron alum or ferric sulphate) do give initially some sort of a blue colouration, but which vanishes again at once and goes very rapidly over into blackish-green, then yellow and finally into orange. A stable blue colour is produced by treating pyrogallol with ferrous salts, e.g. ferrous sulphate, either pure or containing a minor portion only of ferric compounds.

Gallic acid, on the other hand, yields a stable blue colour with ferric compounds which property is shared by derivatives of gallic acid such as tannic acid and chebulinic acid, whilst with ellagic acid the colouration seems to be only faint.

Ferrous salts do not cause any colour change with gallic, ellagic, chebulinic or tannic acids.

Various Plants containing so-called "Mixed"-Tannins.

Bablah
Badan
Cyprus Sumac
Filao
Maletto
Wandoo.

Bablah.

Acacia arabica (Lam.) Willd. of the family Leguminosae, India, Sudan, Senegal. Also called Babool or Sant. Bark and pods contain tannin in appreciable quantities, the bark up to 20%[268]) of flavotannin, whilst the pods (also called Gonakie or Garad) possess up to 30%[269]) and more of a "Mixed" tannin which gives the following reactions :

Fission product : Protocatechuic acid.
With acids : "Reds," gallic and ellagic acids.
Ferric salts : Blue to violet.

The pods yield solutions which are liable to rapid fermentation and seem to contain some appreciable percentage of sugars.[270]) Whether the latter are only part of the non-tannins or whether the tannin itself has a sugar constituent does not seem to be known.

The tannin in the bark produces a harsh and rather dark leather, whilst the pods make a soft, plump and very light coloured leather.[271])

In Northern India, Bablah has been largely displaced by Wattle bark, although it is claimed to be a superior material and to yield extracts with up to 51% tannin.[272])

74

Badan.

Bergenia crassifolia (L.) Fritsch (Megasea crassifolia) of the family Saxifragaceae. Siberia. The roots are stated to contain from 15 to 22% [273]) tannin, and in exceptional cases 25 to 26%. Leaves and stems too possess a considerable quantity of tannin which is said to be between 17 and 25%.

Belavsky and Polansky [274]) state that Badan tannin resembles the tannin in oak bark, i.e. is both a " catechol " and a " pyrogallol " tannin. The leaves are said to contain up to 9% sugar. [275])

Cyprus Sumac.

Leaves of Pistacia Lentiscus L. of the family Anacardiaceae. Also called Lentisco. The leaves are frequently used as an adulterant of leaves of Sumac proper (Rhus coriaria). Tannin content up to 19%. [276])

On heating with acids, " Reds " are produced. The tannin also condenses with formaldehyde to an insoluble body. On fusion with caustic, phloroglucinol and gallic acid are produced, but no protocatechuic acid. [277])

Gives a blue colouration with iron salts.

A small quantity of myricetin accompanies the tannin [277]) (0.15%).

Perkin and Wood [277]) state that a certain quantity of a gallo-tannin is present.

Leaves of a related species, viz. of Pistacia atlantica Desf. yielded a liquid extract with 22.2% tannin, 19.2% nontannins and 1.7% insolubles. [278])

Filao. (Australian Pine).

Bark of Casuarina equisetifolia L. of the family Casuarinaceae, containing up to 20% tannin. [279]) Ceylon, Reunion, Java, Australia.

This tannin has been investigated more closely and a monomolecular catechin has been isolated and identified to which the name Casuarin [280]) has been given of the following structure :
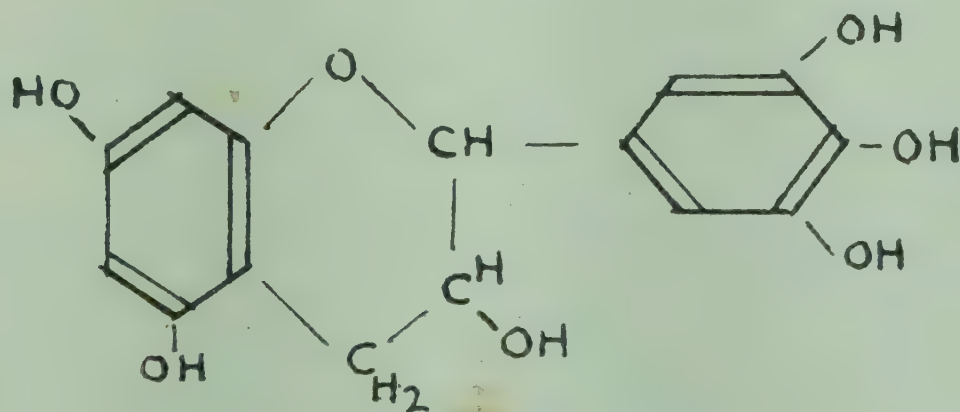
Casuarin (Pentahydroxyflavanol)

The dyestuff myricetin accompanying the tannin has been identified with the following composition :
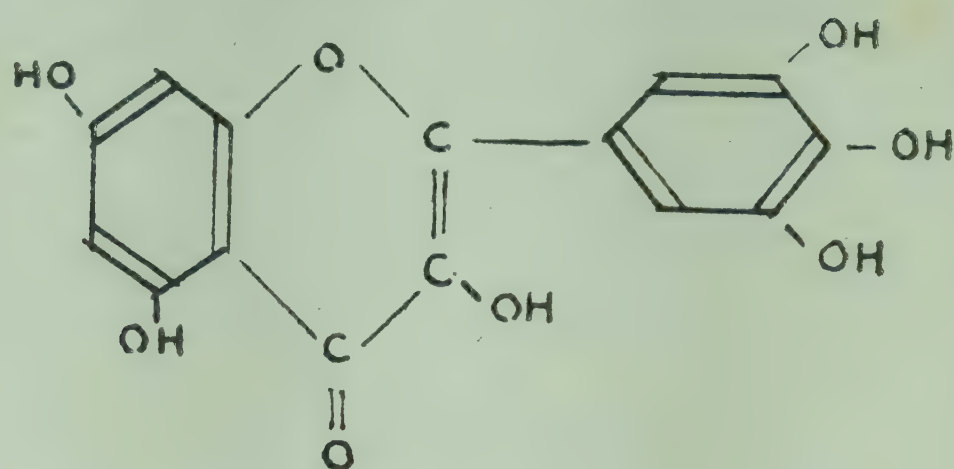
= Myricetin (Pentahydroxyflavonol)

The tannin forms " Reds " and on fusion with alkali, yields phloroglucinol and gallic acid, but no protocatechuic acid.

It gives a blue colouration with ferric salts.

Maletto.

Bark (also called Mallet bark) of Eucalyptus occidentalis Endl. of the family Myrtaceae, Western Australia.

The bark is stated to contain up to 52% tannin which is easy to extract.[281])

Two other Eucalyts are closely related to Euc. occidentalis, viz. Euc. astringens Maiden and Euc. citriodora Hook are sometimes referred to as varieties of Euc. occidentalis. The bark of Euc. astringens (Brown or Red Mallet) is reported to show up to 45.4%[282]) tannin, whilst samples of Euc. citriodora (Lemon-scented Gum) contained 17.3%.[283]) So-called " Gum " of cultivated Euc. citriodora, however, was found to contain 48.2% tannin.[284])

C. O. Williams[282]) states that Euc. astringens Maiden has been cultivated on a small scale in South Africa, and the bark may possess up to 45% tannin.

At the beginning of this century, large quantities were exported, but the supplies were soon almost exhausted.[285])

The tannin in Mallet bark seems to be of the same kind as that in Cyprus Sumac and in Filao. It yields " Reds " with acids and phloroglucinol and gallic acid with alkali, and on dry distillation pyrogallol.[286])

Maletto tannin gives a blue colouration with ferric salts.

Maletto infusions in screened ultra-violet light, impart to cotton wool impregnated with normal analytical solutions, a brilliant blue fluorescence and when the solution is rendered alkaline prior to moistening, a dull mauve fluorecsence. Maletto thus gives a fluorescence almost similar to that of Spruce and Larch tannins.

Wandoo.

Wood and bark of Eucalyptus redunca Schau. of the family Myrtaceae. Western Australia. The tannin in the wood is said to be from 8 to 13% and in the bark from 13 to 21%.

J. R. Blockey, C. H. Spiers and H. G. Beverley[287]) state that the material behaves like a mixture of pyrogallol and catechol tannins, the proportions of the latter being small.

Our own findings seem to show that the reactions are principally those of flavotannins, mixed in the wood with a fairly large proportion of gallotannin, whilst the bark seems to contain less of the latter.

Aqueous infusions of the wood, both untreated and after heating with acid and formaldehyde and filtration, give a deep blue colour with ferric salts. The colouration with bark infusions is less intense. Heating with acids only produces " Reds."

Filtered ultra-violet light imparts a brilliant violet fluorescence to cotton wool soaked in aqueous Wandoo wood infusions and a light blue fluorescence to cotton wool soaked in alkaline solutions. Presence and nature of dyestuffs in Wandoo wood would be worth studying.

Solid extracts are made on a commercial scale from this material and sold as " Myrtan "-extracts. Whilst formerly apparently bark only was used for this purpose, recently both wood and bark seem to be extracted simultaneously. The extract shows mainly the features of the tannin in the wood, i.e. those of a " Mixed " tannin and imparts a deep blue fluorescence to cotton·wool.

The moulding capacity of Wandoo wood moulding powders is low and the property of catalytically promoting the thermosetting of resin-forming components is poor. The flow is bad and the mouldings actually obtained lack strength, probably due to the presence of pyrogallol nuclei and/or gallic acid derivatives, in conjunction perhaps with a comparatively low tannin content.

In immature bark, J. C. Watson and G. S. Tarboton[288]) found 8.4% tannin and 14.35% non-tannin, i.e. only 0.585 tannin per unit of non-tannin. They confirmed the predominence of flavotannin with a possible amount of gallotannin. Their sample of bark seemed to contain a high percentage of gallic acid as constituent of the non-tannins and they considered the possibility that this gallic acid might during maturing perhaps increase the proportion of gallotannin in the tannins. Such a conversion of gallic acid into tannin would reduce the amount of non-tannins and so would raise the tannin-to-nontannin quotient which in mature bark has in general been found to lie between 2 and 3 and sometimes to be even higher than 3.

TANNINS OF THE BRAZILIN TYPE

Almost without exception all tannins of which the constitution is at least partly known are based on gallic acid or on flavane compounds or on derivatives of these two classes of chemical substances.

Among the few products that fall outside this classification, Brazilin and Haematoxylin may be mentioned to which a certain, but low tanning capacity is ascribed. They occur in a few members of the family Leguminosae.

Brazilin[289]) is found in Brazilwood (Caesalpinia echinata Lam.) and Haematoxylin[290]) occurs in Logwood (Haematoxylon campechianum L.) and in Saraca indica L. Both are crystalline and therefore of comparatively low molecular weight; they are used only as dyeing matters. Their constitutions are very similar to each other, almost identical, but for the fact that haematoxylin possesses one hydroxyl group more than Brazilin.

Their structural formulae are probably as follows:

Brazilin[291])   Haematoxylin[292])
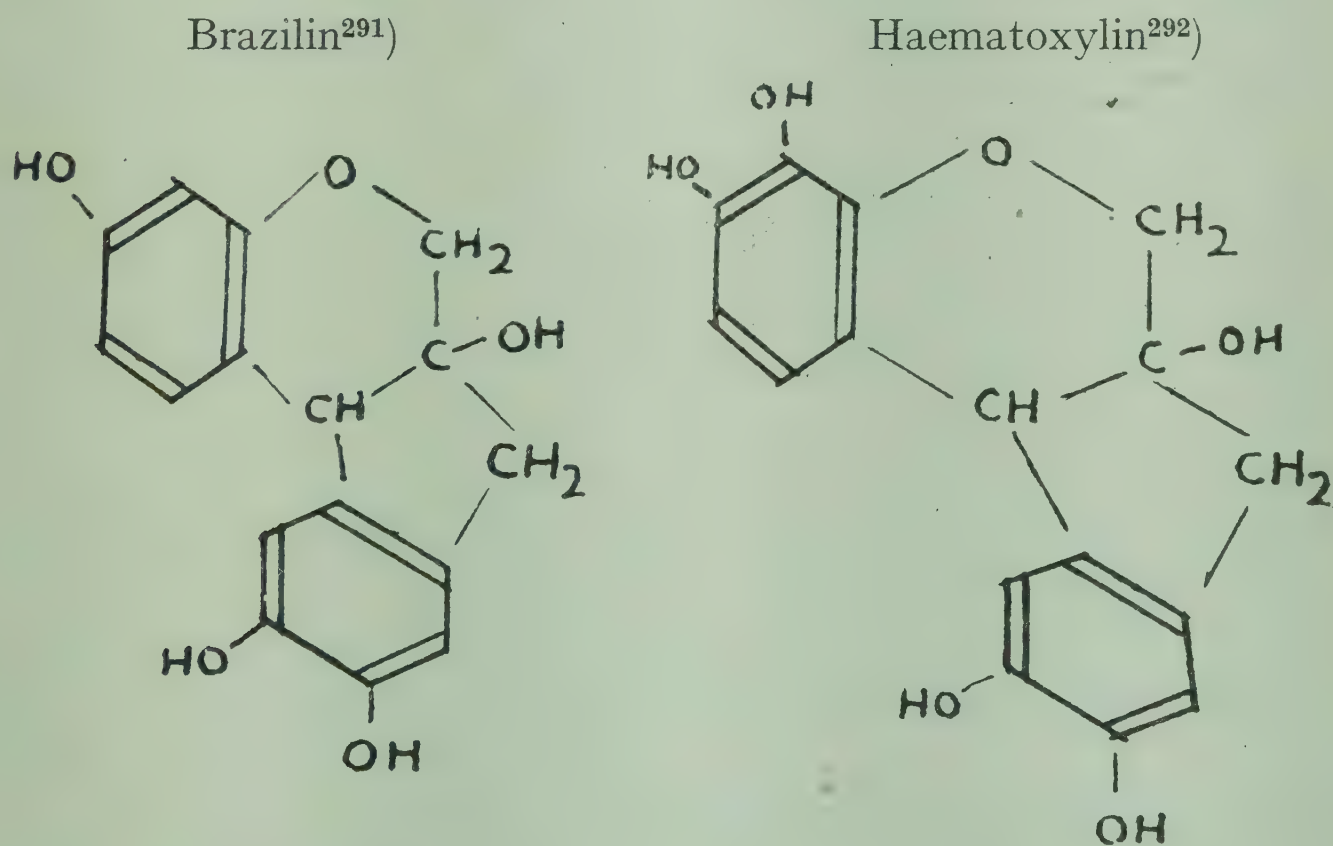
Their constitutions are noticeably very similar to those of catechin or of flavane, the main difference being that the second benzene ring is not attached to the carbon atom nearest to the oxygen bridge, i.e. not in the 2-position as it is the case in catechin and in other flavane compounds, but to the carbon atom in the

79

3-position and that another ring closure has been effected between this second aromatic nucleus and the carbon atom in the 4-position.

The leaves of logwood have been found to contain myricetin.

Haematoxylin on fusion with alkali yields pyrogallol[293]) and according to Erdmann and Schultz also formic acid.

Ellagic acid has been isolated from Haematoxylin campechianum[294]).

Both materials crystallise with water of crystallisation and may be obtained colourless; from water containing a small quantity of bisulphite.[293])

According to some authors, haematoxylin is found to be accompanied by true tannins and phlobaphenes.

TANNINS OF UNKNOWN OR
ALMOST UNKNOWN COMPOSITION

Apart from the plants enumerated in the preceding chapters there are hundreds of other plants which contain some kind of tannin in one or more parts of the organism. In Gnamm " Die Gerbstoffe und Gerbmittel " about two hundred more names are given of plants bearing tannin, mainly of unknown constitution. Most probably the number of such tannins is still greater.

The family Guttiferae for instance seems to possess some members which might be worth investigating. Several plants belonging to this family contain quite appreciable amounts of tannin, e.g. Rheedia braziliensis Planch et Triana is said to have 21.6% in the bark,[295]) Calophyllum inophyllum L. (laurel-wood) 8.4% in bark and 8.0% in wood.[296]) Garcinia Hanburyi Hook., the so-called Gamboge tree is also stated to contain some tannin which is however mainly used as a pigment and a drastic purgative, and at the same time to yield a gum resin containing a yellow dye.[297])

Another genus of this family, viz. Hypericum perforatum L. [298])[299]) is said to contain much tannin that colours iron green and both a yellow and a red dye. Quercetin is also stated to be present. [299]) Cerny[299]) asserted that the red dyestuff of the red dots in the petals of Hypericum perforatum was related to the flavone dyes and had the formula $C_{16}H_{10}O_5$.

J. Dekker[300]) found 5-6% tannin in the pericarps of Garcinia Mangostana L. (Mangosteen or Mangistan or Mangoustan), whilst A. Harvey[301]) referred to an examination by Mahen and Matrod who found 13.6% and stated that the tannin belonged to the " catechol " class giving a precipitate with bromine water, a complete precipitation with formaldehyde and acid and a greenish-black precipitate with iron salts.

The latter plant, viz. Garcinia Mangostana contains a dyestuff which does not seem to have such a close relation to the tannin in the same plant as we usually have encountered in the previous chapters. This particular dye, called Mangostin is crystalline, yellow and is said to have the formula $C_{23}H_{24}O_6$ and on fusion with alkali to yield acetic, valeric and benzoic acids and amyl alcohol. It is supposed to have two phenolic hydroxyl groups, one methoxyl group and one or more amyl groups.[302])

The Mango tree of Southern Asia, Mangifera indica L.[303] of the family Anacardiaceae may be included here. The bark is stated to possess appreciable amounts of tannin varying from 3.5 to 20.6%, whilst the seeds are said to contain as much as 8 to 9%. Cattle feeding on Mango leaves produce a yellow pigment, the so-called Indian Yellow (or Piuri) which is mainly composed of salts of euxanthic acid $C_{19}H_{18}O_{11}$—H_2O, a glycuronic derivative of euxanthone $C_{13}H_8O_4$.[304] A certain connection between Piuri and Mangostin, the dyestuff in Garcinia Mangostana was suggested by Schmid,[305] but has not been corroborated.[305]

One group of materials of some limited commercial importance is to be mentioned in this connection, viz. the products called " Kino." These are the dark red or blackish astringent exudations usually of a resinous nature and rich in tannin found on certain trees, and are derived from various plants of different families, e.g. Butea, Pterocarpus and Prosopis of the family Leguminosae, Macaranga of the family Euphorbiaceae, Angophora and Eucalyptus of the family Myrtaceae, Ceratopetalum of the family Saxifragaceae, and Myristica of the family Myristicaceae.[306]

Some of the products marketed as " Kino " are stated to contain as much as up to 82% tannin.[307] Although they find some use as tanning or dyeing agents, their chief application is in medicine as astringents.

Not much seems to be known about their chemical nature. Some seem to contain a catechol nucleus in their structure and to yield catechol, protocatechuic acid and perhaps phloroglucinol.[308] Catechin has been isolated in various modifications from a number of different types of Kino,[309] so that in a few cases a certain relationship to the flavotannins seems to exist.

The flowers of Butea superba Roxb. contain a dyestuff called Butein which on heating with sulphuric acid yields another and very strong dyestuff. Perkin and Hummel called this latter dyestuff Butin. In accordance with the products obtained on fusion with potash, i.e. resorcinol and protocatechuic acid, Perkin and Hummel [310] ascribe to these two dyes the following structural formulae which shows a distinct relationship to flavane :

Butein.

82
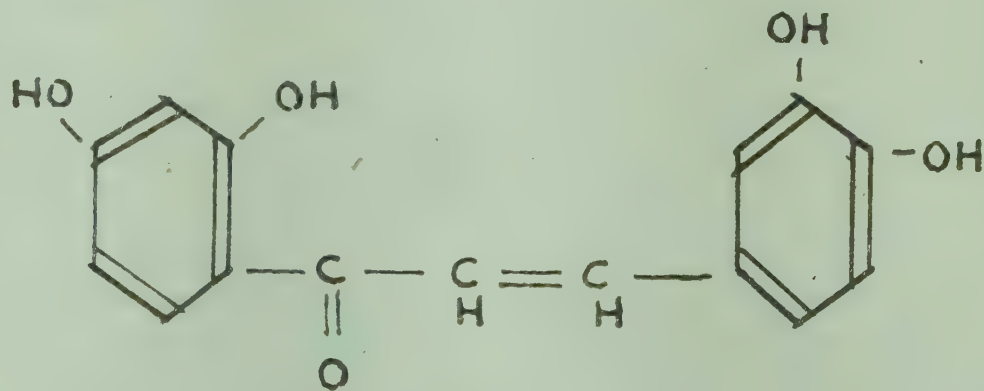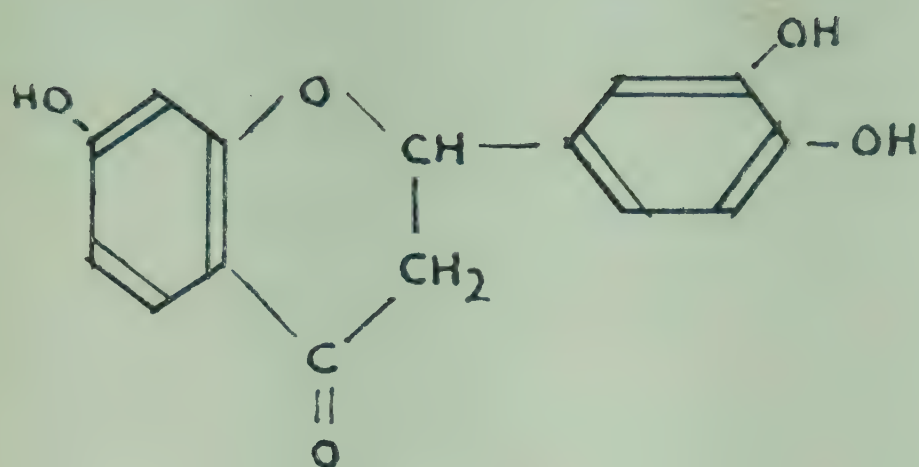
Butin.

The interest in the chemical nature of the tannins contained in this group will possibly be stimulated in accordance with growing technical importance of the single plants. For the time being, however, it would be a more interesting task to attempt to clear up the manifold obscurities in the chemical structure of the more important tannins only.

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APPENDIX

Analytical composition of specific samples of tanning materials, on a 10% moisture basis.

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Common Name.	Botanical Name.	Part of Plant.	Tannins. %	Non-Tannins. %	In-Solubles. %	Fibre. %	Analyst.
Chinese Galls	Rhus chinensis Mill	Galls	64·9	10·1	1·5	13·5	Forestal Co.
Turkish Galls (=Aleppo)	Quercus infectoria Olivier	Galls	64·0	11·9	1·5	12·6	Forestal Co.
Sumac (Sicilian)	Rhus coriaria L.	Leaves	25·7	18·1	1·1	45·1	Forestal Co.
Staghorn Sumac	Rhus typhina L,	Leaves	22·7	19·4	1·6	46·3	See Ref. No. 56
Dwarf Sumac	Rhus copallina L.	Leaves	32·2	19·2	1·4	37·2	,, ,, ,,
White Sumac	Rhus glabra L.	Leaves	28·1	20·2	1·3	40·4	,, ,, ,,
Valonia	Quercus Aegilops L.	Fruit cups	30·1	14·2	1·1	44·6	Forestal Co.
Tea	Camellia sinensis (L.) O. Kuntze	Dried Leaves	9·3	20·0	6·8	53·9	Forestal Co.
Tara	Caesalpinia spinosa (Mol.) Kuntze	Pods (powder)	55·8	16·7	1·1	16·4	Forestal Co.
Dhawa	Anogeissus latifolia Wall	Young twigs and leaves	Abt. 30	Abt. 16			G.—p. 310
" Sumac "					17·8		H.—p. 30
Guarana	Paullinia Cupana H.B. & K.	Pods (Avge)	48·8	23·4	52·1		G.—p. 231
Mangue	Laguncularia racemosa Gaerth. f.	Leaves	21·1	16·8	45·3		Stather Ref. 255
		Bark	30·5	14·2			
Takaout	Tamarix aphylla (L) Lanza	Galls	32·4	15·0	4·9	37·7	Forestal Co.
Myrobalam	Terminalia chebula Retz	Fruits	34·1	14·8	5·1	36·0	Forestal Co.
Divi-Divi	Caesalpinia coriaria (Jacq.) Willd.	Pods	44·6	16·9	0·3	25·2	Forestal Co.
Teri	Caesalpinia digyna Rottl.	Pods (avge)	49·8	15·3	24·9		G.—p. 200, average
Summer Oak	Quercus robur L.	Bark	11·6	8·2	0·2	70·0	Forestal Co.
	,, ,,	Wood	9·2	2·4	0·1	78·3	Forestal Co.
Cork Oak	Quercus suber	Bark	16·9	10·5	0·1	62·5	A. Russell, J.A.L.C.A. 1944, 177.
Willow oak	Q. Phellos L.	Bark	9·1	15·9	65·0		ditto
Chestnut oak	Q. montana Willd.	Bark	9·7	6·1	74·2		Forestal Co.
Chestnut	Castanea sativa Mill.	Bark	6·8	1·4	0·2	81·6	Forestal Co.
,,	,, ,,	Wood	13·4	1·8	0·5	74·3	Forestal Co.

Common Name	Botanical Name.	Part of Plant.	Tannins %	Non-Tannins %	In-Solubles %	Solubles %	Fibre %	Analyst.
Algarobilla	Caesalpinia brevifolia (Clos.) Baill.	Pods	44·7	22·8	2·2		20·3	Forestal Co.
Guayacan Itin.	Caesalpinia melanocarpa Griseb.	Pods	14·8	1·4				G.—p. 304
		Wood	13·5		1·9		73·2	Forestal Co.
Gambier	Uncaria Gambir (Hunt) Roxb.	Leaves	13·0	7·8		69·2		H.—p. 28
Quebracho	Schinopsis Lorentzii (Griseb.) Engl.	Wood	23·6	2·9	3·9		59·6	Forestal Co.
White Quebracho	Aspidosperma Quebracho blanco Schlecht	Leaves	4·0	10·5	0·5		75·0	Forestal Co.
Tizerah	Rhus pentaphylla Desf.	Wood	28·6	3·6	1·8		56·0	Forestal Co.
Urunday	Astronium Balansae Engl.	Sapwood	2·6	2·6	0·1		84·7	Forestal Co.
,,	,,	Wood	13·7	2·2	1·2		72·9	Forestal Co.
,,	,,	Bark	8·9	4·0	2·3		74·8	Forestal Co.
Black Wattle	Acacia mollissima Willd.	Bark	36·1	11·7	1·2		41·0	Forestal Co.
Green Wattle	Ac. decurrens (Wendl.) Willd.	Bark	36·6	10·8			37·2	Forestal Co.
Silver Wattle	Ac. dealbata (Page) Link	Bark	19·1	11·3		42·6		W.—p. 7
Golden Wattle	Ac. pycnantha Benth.	Bark	40·8	10·4		59·6		H.—p. 53
Saligna Wattle	Ac. saligna Wendl.	Bark	21·5	8·8		38·8		W.—p. 13
Mangrove	Not classified specimen	Bark	41·2	9·9	1·7	59·7		W.—p. 17
Spruce	Picea Abies (L.) Karst	Bark	16·2	10·1	1·8		61·9	Forestal Co.
Hemlock	Tsuga canadensis (L.) Carr	Bark	14·8	8·3	1·0		65·9	Forestal Co.
Larch (European)	Larix decidua Mill.	Bark	11·6	5·9	0·6		71·9	Forestal Co.
Larch (Japanese)	L. sibirica Ledeb.	Bark	21·2	11·4	1·8		55·6	Forestal Co.
Willow	Salix viminalis L.	Bark	11·8	8·1		70·1		G.—p. 286
Avaram	Cassia auriculata L.	Bark	22·0	14·1	2·4		51·5	Forestal Co.
Alder	Alnus glutinosa (L.) Gaertn.	Bark	9·1	13·9	0·9		66·1	Forestal Co.
Algarrobo	Prosopis nigra Hieron	Wood	11·1	2·4		76·5		Forestal Co.
Canaigre	Rumex hymenosepalus Torr.	Rhizomes	31·8	18·3	2·9		37·0	Rogers and Russell, J.A.L.C.A. 1944, p. 425
Cu-Nao	Dioscorea atropurpurea Roxb	Roots	42·5	5·7	9·1		32·7	Forestal Co.
Elandsbean	Elephantorrhiza Burchellii	Roots	21·7	21·8	5·5		41·0	Natal T.E. Co.
False Acacia	Robinia pseudoacacia L.	Bark	7·2	4·5		78·3		G.—p. 281
,,	,,	Heartwood (Young Tree)	5·7	3·1		81·2		G.—p. 281

94

Common Name	Botanical Name.	Part of Plant.	Tannins. %	Non-Tannins. %	in-solubles. %	Fibre. %	Analyst.
Gedari	Rhus oxyacantha Cav.	Bark	18·3	6·7	65·3		J.A.L.C.A. 1942, p. 252 (Filter Method).
Kliphout	(Rhus Thunbergii Hook) Heeria argentea (E. Mey) Meisen.	Bark	35·0	17·7	37·7		W.—p. 42.
Ironwood of Malabar	Hopea parviflora Bedd.	Bark	25·4	5·9	58·7		Bull. 27, p. 3 Dept. of Industries, Madras, 1929.
Redwood	Sequoia sempervirens (Lamb) Endl.	Bark	4·4	9·8	0·4	75·4	Forestal Co.
	„	Wood	2·5	3·0	0·8	83·7	Forestal Co.
Sanya	Copaifera Mopane J. Kirk	Wood	11·1	4·4	2·0	72·5	Forestal Co.
„	„ „ „	Bark	16·6	5·7	1·5	66·2	Forestal Co.
Rhodesian Teak	Baikiaea plurijuga Harms.	Bark	26·2	8·7	2·0	53·1	Forestal Co.
Bablah	Acacia arabica (Lam.) Willd.	Bark	16·9	10·0	2·7	60·4	Forestal Co.
„		(Garad Pods)	27·9	19·6	0·8	40·4	Forestal Co.
Badan	Bergenia crassifolia (L.) Fritsch. from Siberia	Roots	26·2	23·2	0·2	40·4	Forestal Co.
„	„ „ grown in England	Roots	20·0	29·5	7·2	33·3	Forestal Co.
	„ „	Leaves	7·7	24·0	0·1	58·2	Forestal Co.
var.	Bergenia cordifolia grown in England	Roots	14·5	27·9	8·0	39·6	Forestal Co.
	„ „ „	Leaves	10·5	35·2	0·2	44·1	Forestal Co.
Cyprus Sumac (Lentisco)	Pistacia Lentiscus L.	Leaves	14·1	17·2	2·6	56·1	Forestal Co.
Filao (Australian Pine)	Casuarina equisetifolia L.	Bark	15·3	3·7			G.—p. 314
Maletto	Eucalyptus occidentalis var. astringens Maiden	a) Bark	43·6	11·6	34·8		W.—p. 22
	ditto.	b) Bark	28·0	10·9	51·1		P. Chambard. Ref. 283.
	Eucalyptus occidentalis var. citriodora Hook	Bark	17·3	7·8	64·9		ditto.
Wandoo	Eucalyptus redunca Schau.	Wood	13·1	4·1	2·4	70·4	Forestal Co.
„	„ „	Wood	11·4	4·0	2·8	71·8	Forestal Co.
„	„ „	Bark	16·2	8·6	0·3	64·9	Forestal Co.
„	immature tree . . .	Bark	8·0	13·8	1·9	66·3	Natal T.E. Co.
Logwood	Haematoxylon campechianum L.	Wood	7·9	6·3	75·8		H.—p. 172
Mangosteen	Garcinia Mangostana L.	Fruit Pericarp	14·2	15·3	60·5		H.—p. 43
Kino. from:—	Eucalyptus siderophloia Benth.		78·8	4·3	6·9	0·0	H.—p. 41.

BOTANICAL INDEX

97

99

ERRATA.

Page 19. Read : Paullinia Cupana H.B. and K.
  ,,   19   ,,   Laguncularia racemosa Gaertn. f.
  ,,   21   ,,   Caesalpinia coriaria (Jacq.) Willd.
  ,,   22   ,,   Caesalpinia brevifolia (Clos.) Baill.
  ,,   37   ,,   Uncaria Gambir (Hunt.) Roxb.
  ,,   67   ,,   Heeria argentea (E. Mey.) Meissn. (Rhus
                      Thunbergii Hook.)
  ,,   81   ,,   Garcinia Hanburyi Hook. f.
  ,,   93   ,,   Common name.